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Molecular Modeling of Rigid-Rod Polymers Structures Dominated by Electrostatic Interactions

(From 1 October 2002 to 30 September 2005 for 36 months)

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14. ABSTRACT

This report results from a contract tasking Institute of Macromolecular Compounds of Russian Academy of Science as follows: PBO, a rigid rod polymer developed by the Air Force Materials Laboratory and now commercially available from Toyobo, has considerable promise for applications as separator membranes in advanced fuel cells and batteries. In such applications, the performance of the membrane is intimately related to the structure of the polymer. In PBO as well as any other polymer used to provide a pathway for ionic conduction, electrostatic interactions are likely to play a dominant role in defining that structure. PBO is a lyotropic liquid crystalline polymer which is soluble only in very strong acids, from which it is processed into fibers or films. Electrostatic interactions may play a very large role in their structure formation by virtue of the charged groups on the polymer itself and the small counter-ions which accompany them. Understanding these interactions may ultimately provide a means of tailoring the morphology which the polymer adopts. We propose to undertake a molecular modeling study of the effect of strong acids on the structure and properties of PBO in solution and bulk state by applying the molecular mechanics approach. Such studies are necessary before larger scale molecular simulations addressing the physical processes underlying of the development in the processing membranes and fibres of the fibrillar structure can be undertaken.

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- **References**
- **List of published papers and reports with abstracts**
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- **Inroduction. Brief description of the work plan : objectives, expected results, scientific approach.**

The initial goal of the project was the investigation of the influence of strong acids on the conformation and structure of PBO molecules in the solution and in the crystalline state. Two main objectives were formulated:

1.Conformation of PBO molecules in solutions of strong acids

2.Effect of the strong acid on the crystalline structure of PBO.

By the project realization it occurred to be more logically to consider the problems of the effect of the acid on the PBO structure not from the side of the process of the dissolution but from the side of the process of the formation of ordered structures from the solution.
The main objectives of the study can be formulated as the following ones ::

1) To study the effect of the protonation on the conformational and deformational properties of the PBO molecules
2) To study the structure formation in PBO solutions in strong acids , in particular:
   a) Aggregation of the PBO molecules in the solution and the mechanism responsible for this aggregation.
   b) Liquid crystalline transitions by the change of the polymer concentration
3) To obtain the structures of the complexes consisting of polymer molecules and acids in conditions of the partial , complete and excess condensation of counterions
4) To calculate the structure of aggregates consisting of these complexes.
5) To calculate the structure of crystal- solvates (phase I and II)
6) To calculate the crystalline structures of the neutral PBO molecules.

The following results were expected to be obtained in frame of this project.

1) Conformational characteristics of PBO chains in solutions of strong acids.
2) Characteristics of the polymer –acid complex.
3) Crystalline structures corresponding to the potential minimum for polymers nontrated and treated by the acid.

The main scientific approach consisted in the application of the methods of computer modeling as well as theoretical models.

- **Methods of the calculation, theories.**

Initially for the solution of formulated above problems only the method of the molecular mechanics was planned . However, it occurred to be necessary to apply also the quantum chemical methods such as the 'ab initio' method and the semi-empirical method AM1, as well as analytical theories developed earlier for similar systems.
In particular , for the problem 1 the quantum mechanical methods were applied. Results obtained allowed to determine the parameters of potentials used later in the MM method.
Problem 2a was solved in the frame of the statistical theory developed earlier for the solutions of polyelectrolytes in polar solvents. The problem 2b was solved on the base of the Onsager theory.

- **Results**

Chapter I. Effect of the protonation on the PBO conformation.

Earlier in [1] for the study of the effect of the protonation on the PBO macromolecule the monomeric unit consisting of one phenyl cycle and one heterocycle (Ph-H). was considered. The obtained conclusions were extended to a polymeric chain .However one have to have in mind that in the completely protonated PBO chains the protonated heterocylcles are situated on both sides of every phenyl cycle.

That is why we have performed the calculations for model molecules with a size exceeding the size of a monomer unit and consisting of three or more of cyclic fragments. Calculations were performed not only for molecules containing twice protonated heterocycles but also for those contaning four protons in a heterocycle. It is known that a heterocycle can join up to 4 protons in such very strong acids as methane sulphonic and chlorine sulphonic acids [5], (protons are connected with oxygen atoms as well). Besides we have considered also patially protonated molecules ,i.e. molecules containing both protonated and nonprotonated heterocycles.

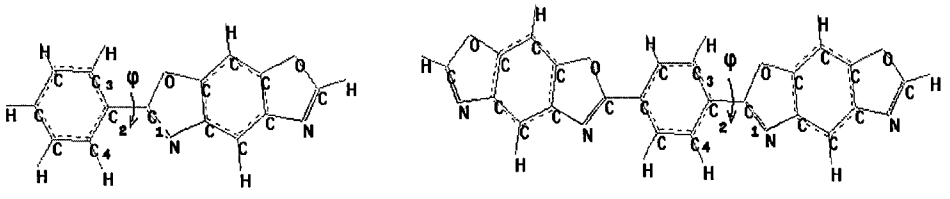
Models and method of the calculations.

Results are obtained for cis-isomeric PBO molecules, i.e containing cis-stereo isomeric heterocycles. In cis stereo-isomers two similar atoms (oxygen or nitrogen) are situated at one side from the long axis of a heterocycle. Cis- isomer was chosen due the technologixal oreferability of this polymer[6-8,9]. Similar calculations were performed for trans-isomeric molecules as well. Obtained results differ only insignificantly.

Calculations were performed for neutral and protonated molecules of different length:

1. Containing one phenyl cycles (Ph) and one heterocycle (H) and corresponding to a repeating unit of PBO (Ph-H)
2. Containing one phenyl cycle and two heterocycles (H-Ph-H))
3. Containing three phenyl cycles and two heterocycles (Ph-H-Ph-H-Ph)

Fig 1 shows chemical structures of (Ph-H) and (H-Ph-H) molecules



a) b)

Fig.1. Structures of molecules modeling a PBO monomer unit (Ph-H) (a) and a fragment of a PBO molecule (H-Ph-H) (b).

Calculations were performed by the semi-empirical quantum chemical method AM1 of the program HyperChem (version 6 of this program).

1.Conformations and barriers of the internal rotation

1.1 Neutral and twice protonated molecules (Ph-H) and (H-Ph-H)

For neutral molecules the addition of the second heterocycle doesn't change the position of the minimum (φ = 0°) and maximum (φ = 90°) of the energy of the internal rotation, as expected. The height of the barrier changes insignificantly (from 2.52 kcal/mole for (Ph-H) to

2.57 kcal/mole for (H-Ph-H). (Fig.2, curves 1, 1'). It allows to restrict ourself by the consideration of the repeating unit by cal;culations of conformations of neutral molecules

For protonated molecules it is not correct. Although positions of the maximum and minimum coincide for molecules H(2+)-Ph-H(2+) and Ph-H(2+) containing twice protonated (for nitrogen atoms) heterocycles, the barrier height (E(90°)-E(0°)) decreases from 7.47 kcal/mole (Ph-H(2+)) to 2.11 kcal/mole (H(2+)-Ph-H(2+)) and became even lower than for a neutral molecule. (Fig 2).

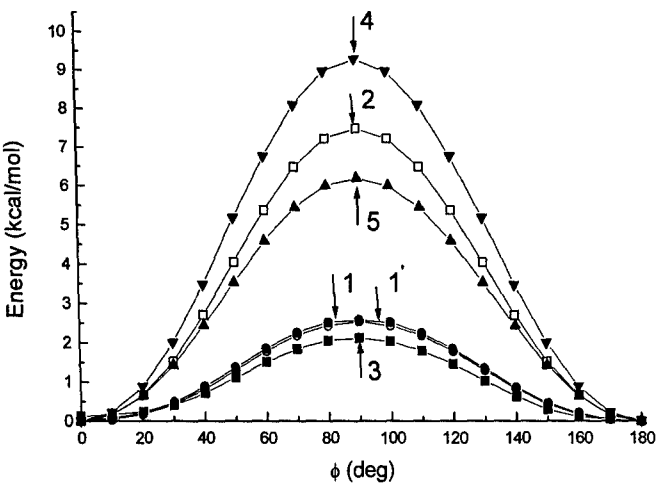


Fig..2.Dependence of the energy on the torsional angle for model molecules Ph-H (1), (H-Ph-H (1'), (Ph-H(2+)) (2), (H(2+)-Ph-H(2+) (3), as well as for (H-Ph-H(2+) for rotations around bonds between phenyl cycle and protonated (4) and neutral (5) heterocycles.

It should be mentioned that at every fixed value of the torsion angle around one of the bonds between cycles the molecule configuration remains to be flat for the second bond.

1.2 Twice protonated molecules (Ph-H-Ph-H-Ph)

To clear up the effect of the chain length similar calculations were performed for (Ph-H(+2)-Ph-H(+2)-Ph) molecule. It was shown that there are two flat conformations ,corresponding to the energy minimum, which differ only by the mutual orientation of heterocycles- oxygen atoms are situated either on the same side or on different sides from the long axis of the molecule.The barrier calculations were performed for a bond between one of the heterocycles and phenyl cycle suruated in the centre of the molecule. It was shown that the barrier height decreases only insignificantly (1.96 kcal/mole) in comparison to H(2+)-Ph-H(2+) molecule. One could expect that the farther increase of the chain length will not change the estimated barrier height.

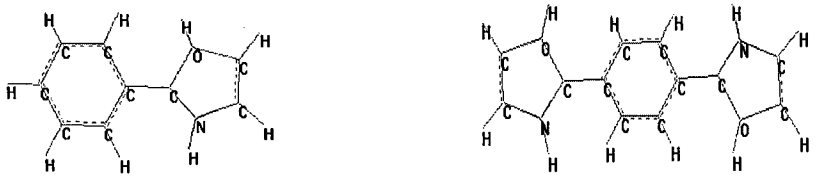
1.3. Four times protonated molecules (Ph-H) and (H-Ph-H)

It was shown in [1] by the optimization of the geometry of the (Ph-H) molecule by the AM1 method, that the addition of the proton to the oxygen atom of the heterocycle is accompanied by the opening of the pentamerous cycle (or by a break of the OC bond). However the ab initio calculations made in the same work have shown the stability of the pentamerous cycle protonated on the oxigen atom. It was concluded that the AM1 parametrization

underestimates the stability of the OC bond for the interactions which arise in the addirionally protonated pentamerous cycle. Our calculations have shown that by the optimization of the geometry (H(4+)-Ph-H(4+) molecule the CO bond doesn't break . It is connected with the significant difference of the distribution of the electronic density in comparison to Ph-H(4+) molecule. .

For the optimal conformations of a (H(4+)-Ph-H(4+) molecule two energy minima were found. One of them is about 0.2 kcal/mole lower than another . These conformations are not flat as for a twice protonated chain : the phenyl cycle is rotated on $\approx$ 50°. from the plane formed by two heterocycles.

We have performed also ab initio calculations of (H-Ph) molecules where as a heterocycle was considered a benzobioxazole corresponding to a heterocycle in PBO molecule в (Fig.1a) and oxazole (Fig.3a), which models a part of a heterocycle in PBO. Moreever similar calculations were performed for (H-Ph-H) molecules with oxazoles as heterocycles (Fig.3b). All heterocycles were protonated both on oxygen and nitrogen.



a) b)

Fig.3.Structures of model molecules containing a phenyl cycle and one oxazole (a), two oxazoles (b) protonated on oxygen and nitrogen atoms.

Energies of molecules were calculated by using the small (RHF/3-21G) and middle (RHF/6-31G) basis.. It was shown that :: for (Ph-H) molecules the energy minima correspond to flat conformations. For H-Ph-H molecule the phenyl cycle is rotated on $\approx$ 50°. from the plane formed by two heterocycles.

Therefore the ab initio calculations have shown:

1) For the modeling of four times protonated PBO molecules one can not use results obtained for a monomer unit because even the conformations corresponding to the energy minimum differ significantly for (Ph-H) and (H-Ph-H) molecules.
2) Results of ab initio calculations agree well with AM1 results for four times protonated (H-Ph-H) molecules

Therefore for the calculation of the potential of the internal rotation the AM1 method was used. Fig..4 shows the dependence of the potential energy of the (H(4+)-Ph-H(4+) molecule on the angle of the rotation around the bond connecting the phenyl cycle and thje heterocycle. The barrier height in this molecule doesn't exceed 1.4 ккal/mole.

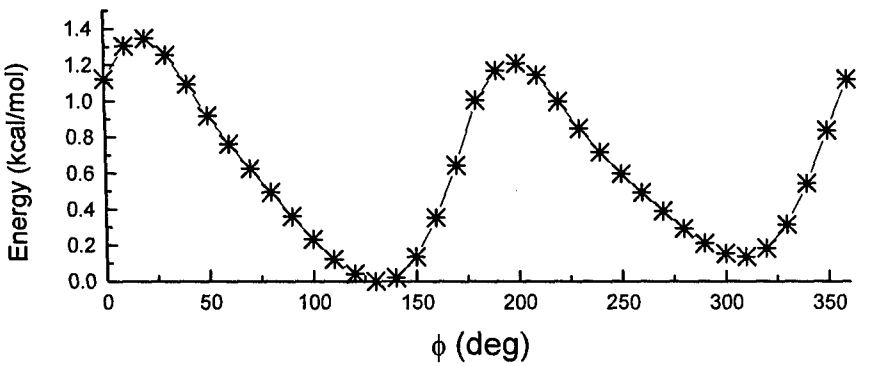


Fig.4 . The dependence of the potential energy of the (H(4+)-Ph-H(4+) molecule on the angle of the rotation around the bond connecting the phenyl cycle and the heterocycle .

So , in this case also the protonation decreases the barrier height in comparison to a neutyral molecule.

1.4. Generalization to longer four times protonated molecules.

The calculation of optimal conformations by the AM1 method were performed for molecules of different length: Ph-H-Ph-H-Ph; H-Ph-H-Ph-H-Ph-H and Ph- H-Ph-H-Ph-H-Ph-H-Ph Addition of new protonated heterocycles gives a very small effect on the barrier height. The values of torsion angles in optimal conformations of the fragment H-Ph-H and of the longest fragment are the same practically. Results of calculations are given in the 2-th quarter report.

Therefore conformational characteristics obtained for a fragment H-Ph-H can be used for the choice of the parameters of the potentials used in the molecular mechanics method.

1.5. Partially protonated H-Ph-H molecule .

All above mentioned results concern to a completely protonated chain. Such a situation is realized by the dissolution in a pure acid or in an acid with small amount of water.are It is known that by the addition of a large amount of water the charged chains are deprotonated [5,9,10]. We have considered the case where one of two hetetocycles in the fragment H-Ph-H is twice protonated and another one is neutral. Again the minimum of the energy corresponds to flat conformations. In this case the height of the barrier of the internal rotation around the bond connecting a phenyl cycle with a protonated heterocycle (Fig.2 , curve 4) increases and became to be equal to ≈ 9.26 kcal/mole. For another bond connecting a phenyl cycle with a nonprotonated heterocycle (Fig.2 , curve 5) the barrier is lower (6.18 kcal/mole), but nevertheless higher than in the neutral molecule..

2. Bond order.

As a main reason of the significant increase of the barrier obtained in [1] by calculations for a PBO monomer unit the loss of the delocalization of the charge was considered arising by the rotation of the phenyl cycle from the position coplanar with the heterocycle. The delocalization is maximal when both cycles are in the same plane and minimal when they are rotated on angle 90°. Change in the degtree of the delocalization can be estimated on the base of the changes of the order of a bond around which the rotation occurs. Fig. 5 shows these changes for different molecules.

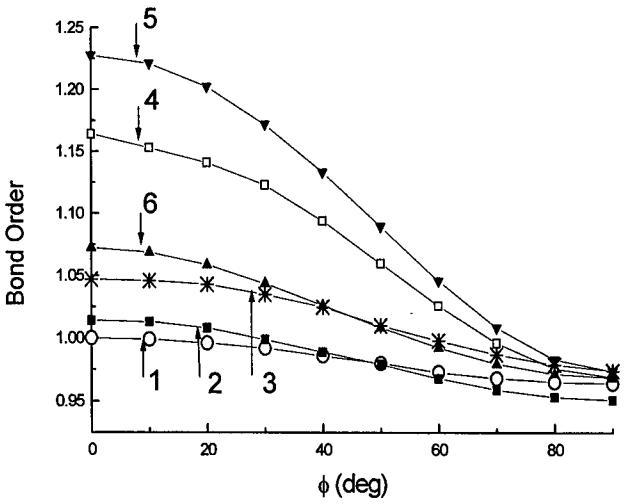


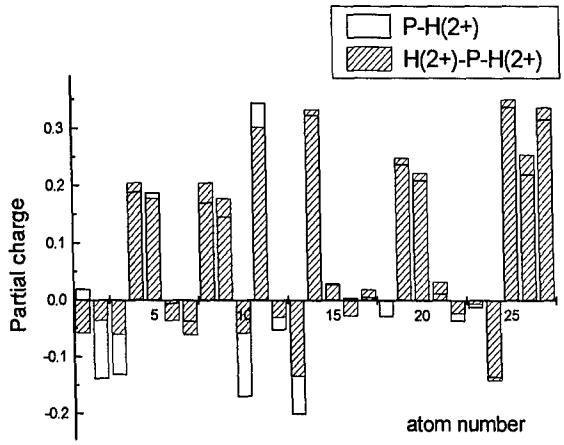
Fig..5. Bond order as a function of the angle of the internal rotation for model molecules (H-Ph-H (1), (H(2+)-Ph-H(2+) (2), (H(4+)-Ph-H(4+)) (3), (Ph-H(2+))(4) as well as for (H-Ph-H(2+) for rotations around bonds between phenyl cycle and protonated (5) and neutral (6) heterocycles

It is seen that instead of the strong increase of the bond order. ($\Delta(0°\text{-}90°)=0.195$) for a ptotonated molecule (Ph-H(2+) which about 5 times larger than for a neutral molecule ($\Delta=0.036$) , for twice and four times protonated molecules H-Ph-H one observes much smaller increase (0.063 and 0.073, correspondingly). This effect appears also in the changes of bond lengths. In a neutral molecule Ph-H the bond length changes from 1.454 Å at 0° to 1.460 Å at 90°. In a twice protonated molecule Ph-H it changes from 1.421 Å (0°) to 1.451 Å (90°).In the same time for twice and four times protonated molecules H-Ph-H the bond length changes from 1.458 Å (0°) to 1.470 Å (90°) and from 1.461 Å(0°) to 1.473 Å(90°) correspondingly.

For partially protonated molecules our calculations predict increase of the barrier of the rotation around both bonds. However the bond order changes significantly (from 1.23 до 1.00) for the first bond (Fig.5, curve 5) and doesn't change practically for the second one (Fig.5, curve 6).

3. Charge distributions on atoms.

The difference in the degree of the delocalization for molecules of different length and its changes by the rotation around the bond between cycles can be seen in the change of the charge distribution on atoms. By the increase of the length of the neutral fragment the charge distribution changed only slightly . For twice protonated molecules the duifferencve between charge distribution for (Ph-H(2+)) and (H(2+)-Ph-H(2+)) is very large ,especially for atoms close to the axis of the rotation (Fig.6)



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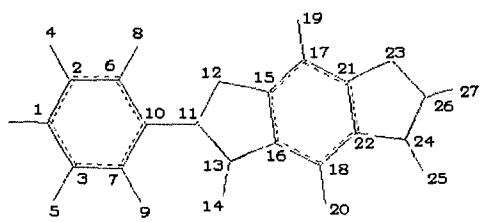

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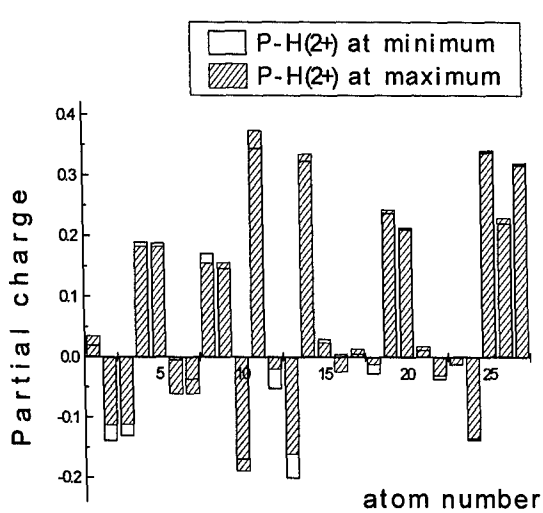
Fig.6.Charge distribution on atoms in molecules Ph-H(2+) and H(2+)-Ph-Г(2+) in conformations corresponding to the minimum of the potential energy of the internal rotation.(a) ,
(b)-atoms numeration.

Changes in the charge distribution on atoms observed by the change of the torsion angle from the value corresponding to the energy minimum to the value corresponding to the energy maximum are most significant for the twice protonated Ф-Г(2+) molecule (Fig.7, a). For twice (Fig.7,b) and four times (Fig. 8) protonated H-Ph-H molecules these changes are small.



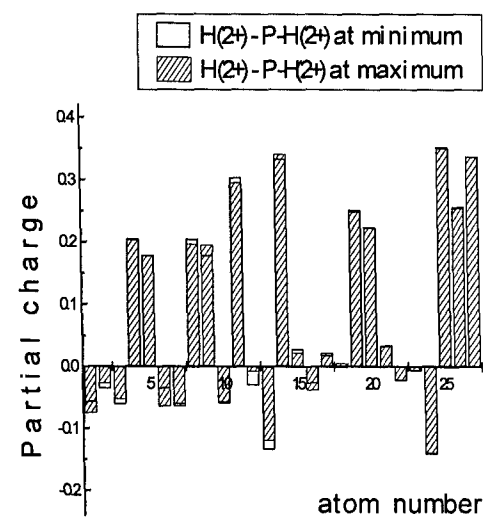


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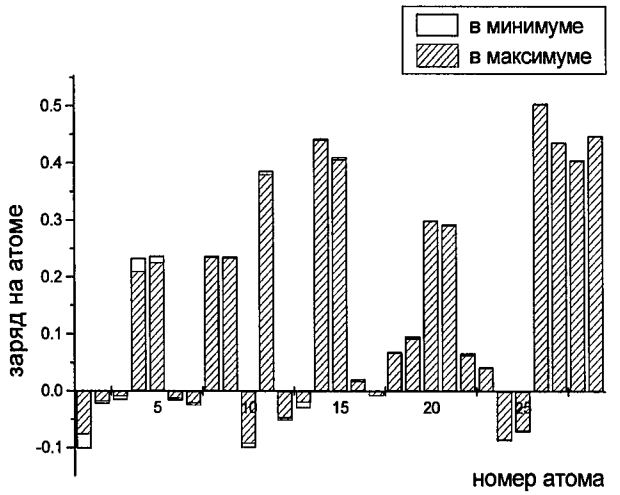
Fig.7. Charge distributions on atoms in a Ph-H(2+) molecule (a) and in H(2+)-Ph-H(2+) molecule (b) in conformations corresponding to the minimum and maximum of the rotation potential.



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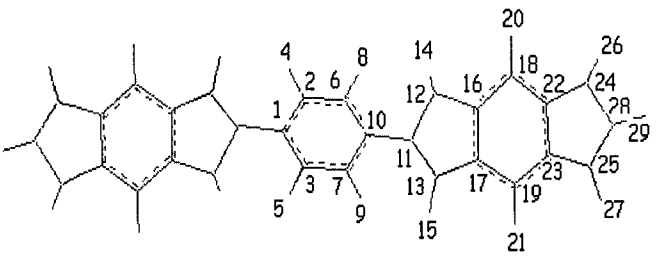


б)

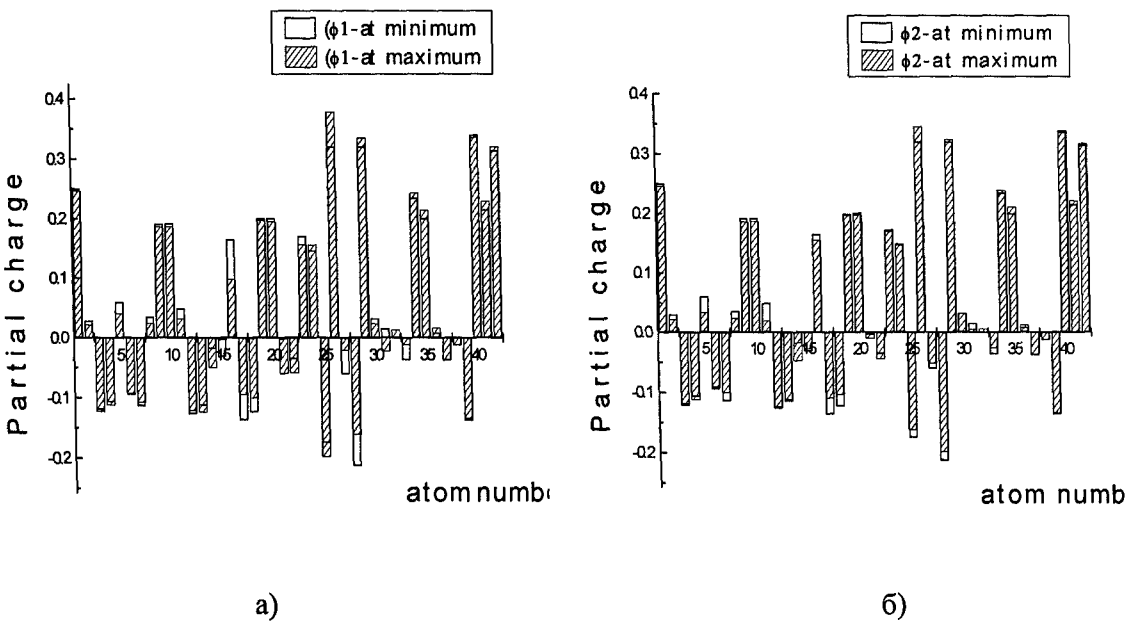
Fig.8. Charge distributions on atoms in a H(4+)-Ph-H(4+) in conformations corresponding to the minimum and maximum of the rotation potential (a). Atom numeration (b)

It seen that the significant part of the positive charge added to the molecule is distributed over hydrogen atoms of the phenyl cycle.. This part (δq) of the positive charge is two times less in the maximum of the energy than in the minimumпри значениях торсионного угла в (from 21% to 11%), for a twice protonated molecule Ph-H(2+) . For H(2+)-Ph-H(2+) and H(4+)-Ph-H(4+) molecules changes of δq are small (from 19.2% to 18.9% and from 11.8% to 11.5% correspondingly).

Therefore the loss of the dolocalization at the protonation is overestimated for Ph-H molecules in comparison to the symmetric H-Ph-H molecule. Nevertheless the values of the change of the bond order for protonated molecules H-Ph-H by the rotation from the energy minimum to the energy maximum exceed such changes for a neutral molecules. One could expect that this factor should lead to some increase of the potential barrier although not sucho strong as was obtained in [1]. However our calculations show that this barrier decreases for

protonated H-Ph-H . As it will be shown in the next section the **coulomb interactions** are the factor leading to this decrease.

For the partially protonated H-Ph-H molecule the changes of the order of two bonds and corresponding loss of the delocalization mentioned above appear also in the changes of the charge distribution by the internal rotation . Charge distributions in the minimum (0°)and maximum (90°) for the first bond (Fig.11, a) differ significantly . In the same time this difference is small for the second bond. (Fig11, b) .



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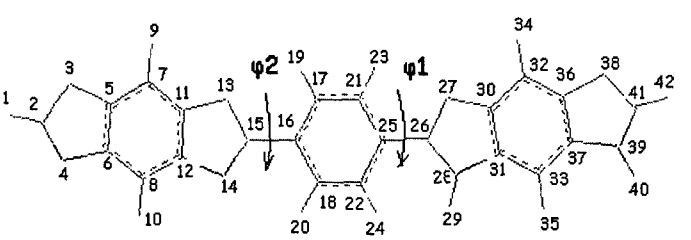


в)

Fig.9. Charge distributions on atoms in a H-Ph-H(2+) molecule for φ**1**(a) и φ**2** (b) in conformations corresponding to the minimum and maximum of the rotation potential. . Atom numeration (c)

4. Coulomb interactions

. Fig.10 shows the dependence of the coulomb energy on the torsion angle for different models. For a neutral H-Ph-H molecule this energy doesn't change practically. For the Ph-H(2+) molecules the energy increases significantly but for H(2+)-Ph-H(2+) and H(4+)-Ph-H(4+) molecules this energy decreases leading to the decrease of the potential barrier comparing to the neutral molecule.

For a partially protonated molecule the electrostatic energy increases sharply for both two bonds by the rotation on the 90° angle (Fig.10, curves 5 and 6), leading to the increase of both barriers of the internal rotation.

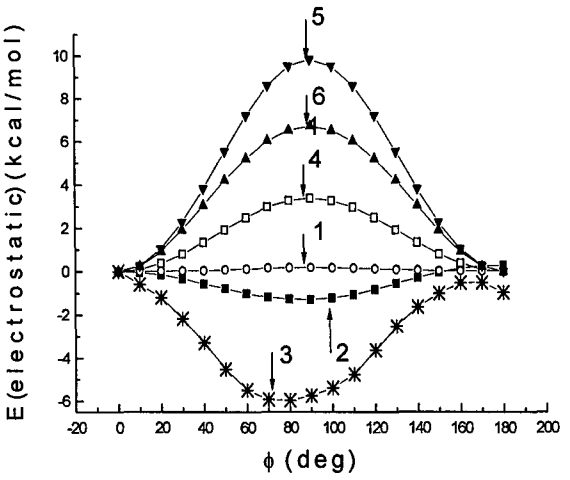
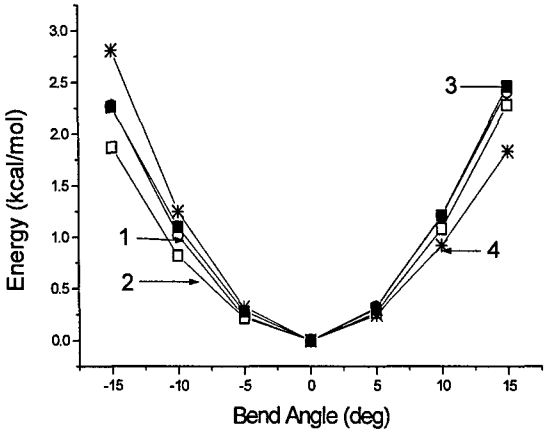


Fig..10. Dependence of the Coulomb energy on the torsion angle for model molecules (H-Ph-H (1), , (H(2+)-Ph-H(2+) (2), (H(4+)-Ph-H(4+) (3), (Ph-H(2+))(4) as well as for (H-Ph-H(2+) for rotations around bonds between phenyl cycle and protonated (5) and neutral (6) heterocycles.

5. Bending defiormations .

Fig.11 shows the energy dependence on the bending angle for a neutral and charged molecules. Positive values of the angle correspond to the bending deformation near the carbon atom of the heterocycle. Negative values correspond to the bending deformation near the carbon atom of the phenyl cycle. For neutral molecules H-Ph and H-Ph-H results coincide. Moreover the curve is the same for H(2+)-Ph-H(2+) molecule. For the four times y protonated molecule the asymmetry is observed: the resistance to the bending deformation is stronger near the phenyl cycle and weaker near the heterocycle in comparison to the neutral molecule.

a)



b)

Fig. 11 . Bending deformations : (a) a side view of the PBO molecule deformed near the carbon atom of the heterocycle (0° , 5° , 10°, 15°),
(b) dependence of the deformation energy on the bending angle for model molecules: Φ-Γ (1), Φ-Γ(2+) (2), Γ(2+)-Φ-Γ(2+) (3), Γ(4+)-Φ-Γ(4+) (4).

More detailed information concerning the results presented in this chapter is given in 2-th and 3-th quarter reports.

Chapter II. The calculation of the parameters of potentials describing the interactions in a neutral and protonated PBO molecules

MM "force-field" of the program "HyperChem"includes the following potentials:

1) Deformation potential for valence bonds
2) Deformation potential for valence angles
3) Torsion potential,
4) Bending deformation potential
5) Electrostatic potential
6) Non-valence interaction potential

The parameters which are present in the program are related to neutral molecules.Besides some of them are absent. We have calculated the parameters of the deformation and torsion potentials for protonated molecules.

By the AM1 method the conformation energies were calculated as functions of molecularb parameters : valence bonds and angles, torsion angles. The calculated curves were approximated by the corresponding dependences . By such a way the parameters giving the best agreement between curves , calculated by AM1 and MM method were estimated.

1. Elasticity constants for valence bonds

For neutral and twice protonated fragments the elastic constant for all bonds are the same. For a four times protonated fragment elastic constants are lower.

It should be mention that all constants obtained on the base AM1 data occuredvto be lower than those presented in the corresponding set of MM of the HyperChem program.

AM1 curves for some bonds are given in Fig..2,3,4.as examples. Table 1 contains parameters calculated for all bonds.

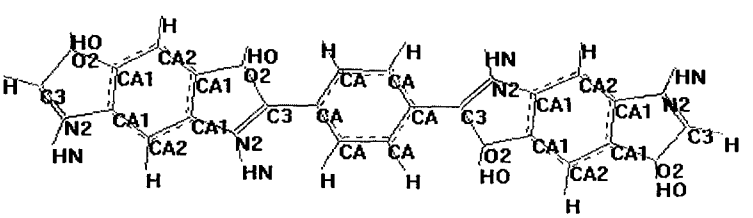


Fig.1. Atoms in a protonated fragment H(2+)-Ph-H(2+)

Expression for the energy of the deformation of a valence bond MM+"HyperChem" set of the interaction potentials.

Energy = 71.94(Kr)(dr)(dr)(1+(cs)(dr)) **(1)**

dr = R-R0

cs = -2.000

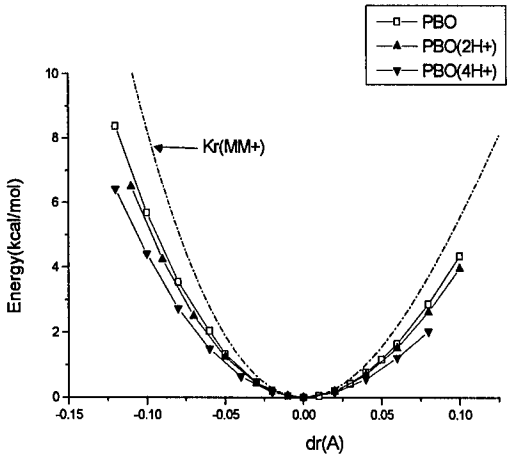


Fig.2 Valence bond CA-C3. Approximation of AM1 curves by (1) gives the following values of Kr:PBO: Kr=6.72 ; PBO(2H+): Kr=6.3; PBO(4H+): Kr=5.1
Kr(MM+'HyperChem')=9.6

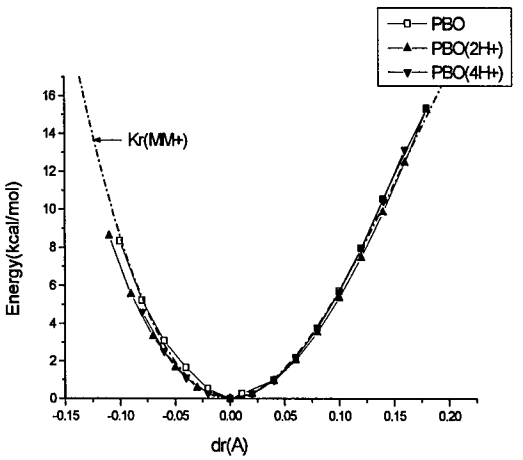


Fig.3 Valence bond C3-N2.
PBO: Kr=10.7 ; PBO(2H+): Kr=9.5; PBO(4H+): Kr=10.1
Kr(MM+"HyperChem")=10.0

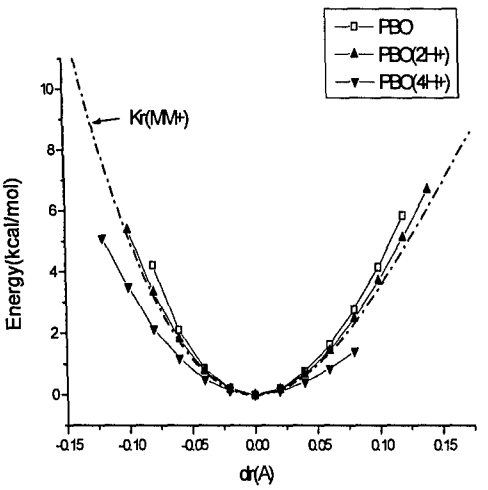


Fig..4. Valence bond CA1-O2.
PBO: Kr=7.7; PBO(2H+): Kr=6.4; PBO(4H+): Kr=4.9 Kr(MM+"HyperChem")=6.0

Table 1.

Kr				
	AM1			MM+
Bond	neutral	2H+	4H+	
Ca-C3	6.7	6.3	5.1	9.6
C3-N2	10.7	9.5	10.1	10.0
C3-O2	5.3	6.5	3.2	6.0
Ca1-O2	7.7	6.4	4.9	6.0
Ca1-N2	7.0	6.9	6.2	10.0
Ca1-Ca1	5.9	6.3	6.3	8.07
Ca1-Ca2	7.6	7.0	7.2	8.07
Ca2-H	5.0	5.0	4.6	4.6
Ca-H	5.7	5.7	4.5	4.6
N2-HN	---	6.0	4.7	5.9
O2-HO	---	---	4.0	
C3-H	5.2	4.5	3.8	4.6
Ca-Ca	7.1	7.1	6.5	8.07

2. . Elasticity constants for valence bonds

. For neutral and twice protonated fragments the elastic constant for all valence angles are the same. For a four times protonated fragment elastic constants are higher All constants obtained on the base AM1 data occurred to be higher than those presented in the corresponding set of MM of the HyperChem program.
AM1 curves for some angles are given in Fig..5,6,7.as examples. Table 2 contains parameters calculated for all angles.

Expression for the energy of the deformation of a valence angles in a MM+"HyperChem" set of the interaction potentials.
:

Eb = 0.043828(Kb/2)(dΘ)(dΘ)(1+sf*dΘ4) (2)**
dΘ = Θ-Θ0 , sf = 0.00700e-5

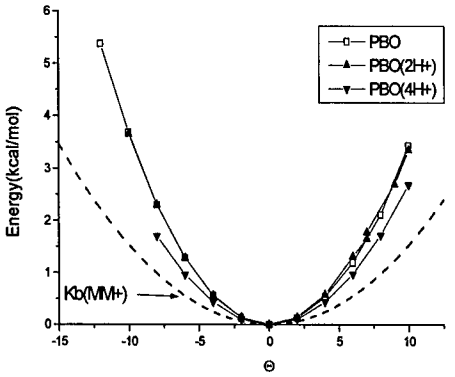


Fig.5. Valence angle CA-C3-O2. Approximation of AM1 curves by (2) gives the following values of Kb: PBO PBO: Kb=1.64; PBO(2H+): Kb=1.54; PBO(4H+): Kb=1.22
Kb(MM+)=0.700

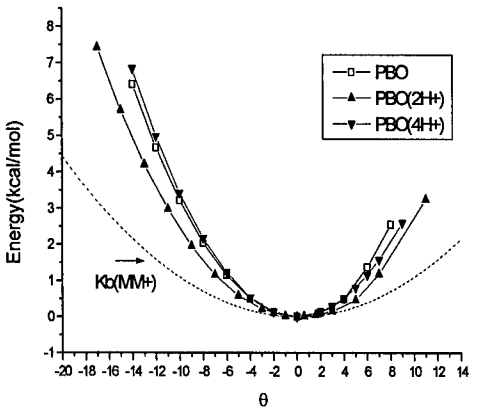


Fig.6. Valence angle CA-C3-N2
PBO: Kb=1.50; PBO(2H+): Kb=1.56; PBO(4H+): Kb=1.16, Kb(MM+)=0.500

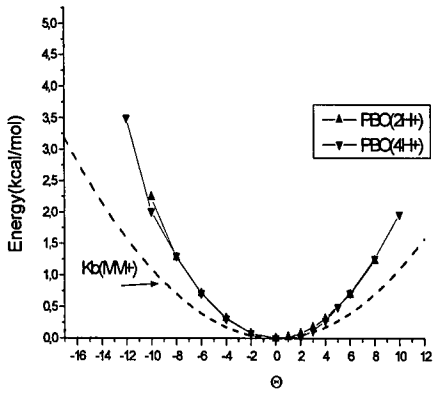


Fig..7 Valence angle C3-N2-HN
PBO(2H+): Kb=1.09; PBO(4H+): Kb=0.93; Kb(MM+"HyperChem")=0.500

Table 2.

Kb				
	AM1			MM+
Bond angle	PBO(neutral)	PBO(2H+)	PBO(4H+)	
Ca-C3-N2	1.500	1.560	1.160	0.500
Ca-C3-O2	1.640	1.540	1.220	0.700
N2-C3-O2	3.460	3.880	2.960	---
C3-O2-HO	---	---	0.540	0.350
C3-N2-HN	---	1.090	0.930	0.500
C3-Ca-Ca	1.620	1.620	1.330	0.430
H-Ca-Ca	1.030	0.960	0.900	0.360
Ca-Ca-Ca	2.350	2.300	2.280	0.430
C3-O2-Ca1	3.950	3.820	3.340	---
O2-Ca1-Ca1	3.770	3.930	3.070	0.700
O2-Ca1-Ca2	3.770	3.930	3.070	0.700
C3-N2-Ca1	3.360	3.930	3.070	0.400
N2-Ca1-Ca1	3.820	3.920	3.470	0.500
N2-Ca1-Ca2	3.820	3.920	3.470	0.500
Ca1-N2-HN	---	1.090	0.930	0.500
Ca1-O2-HO	---	---	0.540	0.350
Ca1-Ca2-Ca1	2.520	2.520	2.430	0.430
Ca1-Ca1-Ca2	2.440	2.400	2.320	0.430
Ca1-Ca2-H	0.930	0.880	0.830	0.430
O2-C3-H	0.840	0.800	0.720	0.540
N2-C3-H	0.730	0.700	0.670	0.300

3. The choice of parameters of torsion potentials.

Expression for the torsion energy in a MM+"HyperChem" set of the interaction potentials.

$$\mathbf{Et = (V1/2)(1+\cos(\phi))+(V2/2)(1-\cos(2\phi))+(V3/2)(1+\cos(3\phi))} \qquad \mathbf{(3)}$$

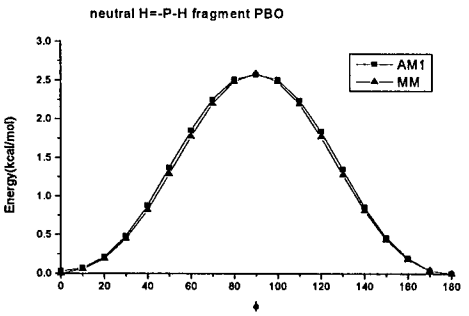


Fig. 8. Torsion energies calculated by using AM1 and MM methods for a neutral Γ-Φ-Γ molecule . Parameters of the torsion potential (3): V1=0; V2=0,94 kcal/mol; V3=0.

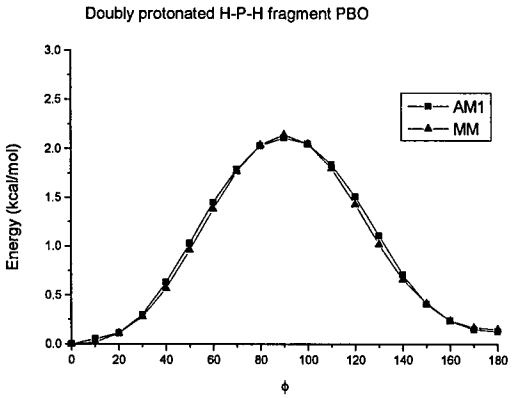


Fig 9. Torsion energies calculated by using AM1 and MM methods for a twice protonated Γ(2+)-Φ-Γ(2+) . Parameters of the torsion potential: V1=0; V2=1.46 kcal/mol; V3=0.

Detailed information concerning results presented in this chapter is given in 1-th and 3-th quarter reports.

Chapter III. Formation of the structure in solutions of PBO in strong acids. The role of the dielectric properties of the medium (dielectric constant) and counterions.

1. Aggregation of polymer chains.

Such polymers as PBO in solutions of strong acids aggregate at definite conditions: either at some polymer concentration(~ 20%), or by addition of a some amount of water.The necessary amount of water increase with decrease of the polymer concentration .It is ~10% at the polymer concentration ~1% -

One of the main questions is a mechanism of this aggregation: the nature of forces responsible for it .

Different mechanisms suggested in the literature [12,13,14,15,16,17] were analyzed.The most suitable occurred to be that [16,17] based on the idea about the formation of ionic pairs and multiplets (tetramers) . Tetramers are formed as aresult of

theassociation of ionic pairs and work similar to crosslinks between polyions. It leads to the aggregation of polyions. In this model the formation of ionic pairs and tetramers are considered as reversible reactions with corresponding association constants. Their values depend on the energy of the interaction of charges which in turn depends on the dielectric properties of the medium. In the solution the dielectric constant is a function of the polymer concentration and decreases with its increase. At some concentration the appearance of the aggregated phase occurs to be possible even in polar solvents ,such as acids..

On the base of this theory [17] we have calculated the phase diagrams of the polyelectrolyte solution with parameters corresponding to the PBO solution in the strong acid. The rigidity of the PBO chain wasn't taken into account.

Two cases were considered:

1) Similar to [17] the association constants for ionic pairs and tetramers were taken to be equal to each other
2) In contrast to [17], the case when these constants are different.

Additionally we have considered the case when the water was added to the solution leading to the appearance of new counterions additional to those formed by the protonation of polymer chains.

1.1 Equality of association constants

Phase diagram were constructed by calculation of polymer concentrations on the boundary of the existence of different phases. The regions of the coexistence were determined from the solution of the system of two equations:Equality of 1.chemical potential and 2.osmotic pressure in both phases .

The phase diagram was constructed in coordinates —solvent quality . Analysis gives three regions:

I – region of the dilute solution where the concentration of ionic pairs and tetramers is small

II – region of the coexistence of the dilute solution and the aggregated state

III - region of the aggregated state .

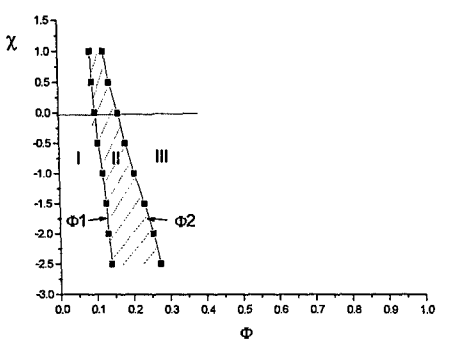


Fig.1. Phase diagram. The region of the coexistence of two phases is shaded..

The coexistence region is very narrow and is situated at low polymer concentrations It gets broader as the quality of the solvent became better. In particular at χ=1.0, i.e. in a poor solvent $\Phi 1$=0.09, $\Phi 2$=0.12, at χ=0 , i.e. in an athermal solvent $\Phi 1$=0.096 And $\Phi 2$=0.16, at negative values of χ, i.e in good solvents , for example ,at χ= -1.0 $\Phi 1$=0.12, a $\Phi 2$=0.2.

These values are in agreement with experimental data.

1.2. Unequality of association constants

For the calculation of association constant of tetramers we took into account that the energy of the interaction of ionic pairs (dipoles) depends on their mutual

orientation. To take into account the non-optimal placement of dipoles of neigbouring chains we included into the expression for the association constant of tetramers the variable parameter $a<1$. Calculations were performed for different values of this parameter corresponding to energy of the interaction which are less than the energy of the formation of the ionic pair. It was shown that the decrease of this parameter the maximum of the distribution of ionic pairs shifts to larger concentrations and the the fraction of tetramers decreases. The region of the coexistence of the dilute and aggregated phases becomes broader , but the position of the lower boundary changes only slightly. The broadening occurs mainly due to the significant shift of the upper boundary to larger concentrations.

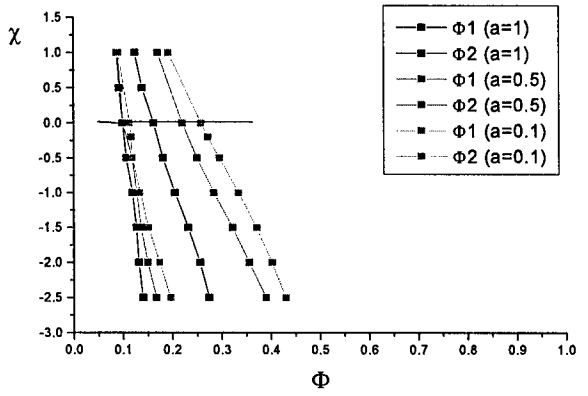


Fig.2 Phase diagram.

1.3. Solution with an excess of counterions.

The water added to the PBO solution in a strong acid is a source of additional counterions. It is believed that at addition of the small amount of water all added water molecules became to be protonated and new acid anions arise. Howere the degree of the PBO protonation doesn't change [11]. These additional anions form also ionic pairs with polymer segments. Our calculations have shown that I this case the aggregated state appears at more low polymer concentrations in agreement with experiment [11].

In more details the model and corresponding calculations are presented in the 5-th quarter report.

2. LC transition in PBO solutions in strong acids.

LC transition in PBO solution was considered in frame of the general theory of LC transitions in polyelectrolyte solutions. Two main effects were considered: Debye screening of electrostatic interactions between charged with the same sign polymer molecules and attraction between molecules due to the interaction of ionic pairs formed by polymer charges and counterions..

We have performed the analysis of the existing theories. The majority of them is based on the use of the second virial approximation. Onsager [18] has shown that the

coulomb interactions lead to the effective renormalization of the diameter of the charged rod depending on the linear charge density, Debye screening and dielectric properties of the medium. LC transition in the solution of charged rods occurs at lower polymer concentrations in comparison to the solution of neutral rods. In [19] the effect of the salt addition was studied. In our salt free case the screening of the electrostatic interactions occurs due to the presence of counterions .

There are also some approaches which take into account correlated manyparticle interactions [20] . They stimulate a weak nematic ordering at very small concentrations. However experimental data show [21]that LC transition in PBO solution occurs at concentrations two order higher than those predicted by the correlation theory.

On the base of results described above we suggested that there are two types of the interactions in the PBO solutions in strong acids: electrostatic repulsion and attraction between ionic pairs. Electrostatic repulsion was considered in the second virial approximation with the coefficient depending on the Debye radius in the system [19]. Electrostatic attraction was considered on the base of the approach [17], based on the ionic pair formation .Dielectric constant was considered to be dependent on the polymer concentration.

2.1. Debye screening of electrostatic interactions.

For the estimation of the Debye radius we have used results obtained for the model of the solution of charged rods [22-25].

I). Expressions for the radius of the screening.
The electrostatic potential depends both on the concentration of rigid rods (polyions) and small particles (counterions)
If the screening only due to polyions was considered the Debye radius changes with the polymer concentration as $c_p^{-1/3}$
If the screening only due to counterions was considered the Debye radius changes with the polymer concentration as $c_p^{-1/2}$
The account of both factors leads to a more complicated dependence.

By the calculation of the Debye radius the following parameters were used:
1.The length of the effective monomer was chosen to be equal to the half of the monomer unit of PBO ($a = 6.15$ Å).
2. Bjerrum length for the strong acid (with $\varepsilon = 60$)
$l_B = 9.33\,\mathring{A}$
3. For twice protonated heterocycles the initial charge per monomer $f_0 = 1$
The effective charge f due to the counterion condensation was calculated by using Oosava equation , [25] .

2) Results
Calculation of the Debye radius were performed for the range of polymer concentrations from 10^{-6} to 10^{-1}.

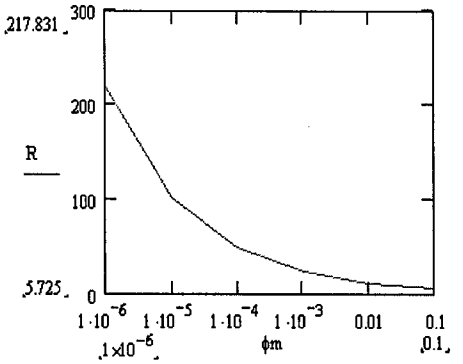


Fig.1. Concentration dependence of the Debye radius due to polyions only

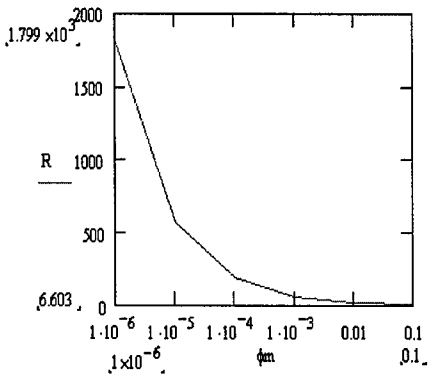
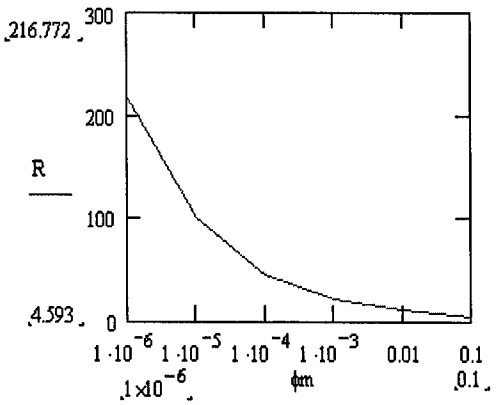


Fig.2. . Concentration dependence of the Debye radius due to counterions only



.Fig.3 Concentration dependence of the Debye radius due to the presence both of polyions and counterions

These results were used later by the analysis of the anisotropic state of the PBO solution.

More detailed information can be seen in the 4-th quarter

2.2. Characteristics of the LC transition.

I). Characteristics of the LC transition in frame of the second virial approximation

For neutral rods with parameter corresponding to PBO molecules the volume fractions of the polymer on the boundary of the coexistence of the isotropic $\Phi 1$ and nematic $\Phi 2$ phases are equal to 0.056 and 0.075, correspondingly. The order parameter inLC phase is **S=** 0.847. For charged rods $\Phi 1=0.0062$, $\Phi 2=0.0074$, and S=0.728. .

2). Characteristics of the LC transition taking into account Debye screening and interactions between ionic pairs.

Above calculations have shown that the LC transition occurs at much lower polymer concentrations than the experiment shows. At these concentrations ionic pairs can not be formed.

.We suggested that the new ordered phase should be formed at higher concentrations when these pairs begin to arise.

The energy of the interaction between ionic pairs was considered to be dependent on the mutual orientation of rods and proportional to s^2 . The system of four equations was solved which includes the conditions of the equality of chemical potentials and osmotic pressures of isotropic and nematic phases and the conditions of the minimum of the free energy .

It was shown that the range of the concentrations where two ordered phases coexist has a lower boundary at $\Phi 1=0.034$, and a higher -at $\Phi 2=0.314$. The lower concentration is close to the experimental value of the concentration of the LC transition of PBO solution [21]. The higher concentration corresponds to the aggregated state. The order parameter of the less concentrated LC phase in the point of the transition is equal to 0.82 , i.e. by the increase of the concentration the growth of the order parameter of the phase I is observed (from 0.728 to 0.82). More concentrated phase II has a larger order parameter **S=** 0.98. .

More detailed information can be seen in our 6-th quarter report

Chapter IV. Internal structures of aggregates phases

As it was shown in the chapter III by the concentration increase in the PBO solution in a strong acid the aggregation of chains is observed [11], due to the formation of ionic pairs [17]. In the system containing PBO, acid and water two intermediate (before the crystallization of neutral molecules) crystal-solvate phases are formed. At definite conditions (> 7% of water) the transition from one phase to another is observed. By farther addition of water the chains are deprotonated , acid molecules are washed out from aggregates and the crystalline phase of neutral PBO is formed. Therefore the complexes polycation+acid anions are formed already in the solution. In the solution the charge of the polycation is compensated only partially ,but by the transition into crystal-solvate phase this charge should be compensated completely.

Our first task was to construct the model of the complex polymer-acid for the cases of the partial and complete counterion condensation (results are presented in the part 1) . The structure of the complex can change by the aggregation and our second task was the study of this effect (part 2). The next step was the calculation of the structure

of the crystal-solvate (results for the phase I are presented in the part 3). Transition from the phase I into phase II is considered in the part 4. Results of the calculations for the phase II are given in the part 5, and of a crystalline structure for neutral PBO molecules –in the part 6.

1. Model of the complex polymer-acid. Partial and complete counterion condensation on the chain. Effect of the condensation on the polyion conformation.

Experimental data about two crystal-solvate phases were obtained [10] for the PBO solution in the polyphosphorous acid (the general formula H (n+2) P (n) O (3n+1)), the polymerization degree of the acid isn't known. Structure investigations don't give answers on the questions about the placements of acid molecules in the cell, about the degree of their deprotonation [10,26], about the number of neutral and deprotonated acid molecules in a crystalline cell. The answer can be obtained only from model calculation and comparison with experimental data..

The calculation of the complex structure were performed for anions of the polyphosphorous acid H (n+2) P (n) O (3n+1) for n= 1 and 2 (anion charge = -1) and n=3 (anion charge = -1 and –2). In the case n=3 the charge = –2 on an anion was obtained as a result of the deprotonation of terminal phosphorous groups. Besides similar calculations were performed for complexes containing not only charged but also neutral acid molecules for cases n=1 and n=2, .

As a chain model the chain consisting of three phenyl cycles and two twice protonated heterocycles was chosen. The protonation of the hetercycles was performed by the addition of protons to nitrogen atoms. Chains contained either cis or trans stereoisomers of heterocycles. Partial and complete counterion condensation were considered ,i.e. the cases when one, two, three and four counterions join to the chain. Most profitable conformations of a protonated chain and deprotonated acid molecule and corresponding charge distributions on atoms were calculated by the AM1 method. The counterion conformation was fixed and all chain parameters were varied. The complex structure was calculated by the MM method. The parameters of potentials used are given in the chapter II.

We present data only the structures of complexes with anions of the orto-phosphorous acid (n=1). For other cases (n=2, n=3) results are similar.

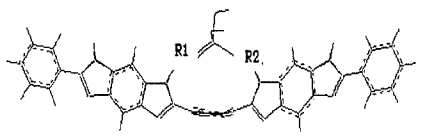
1.1. Cis-stereoisomers.

Partial condensation:

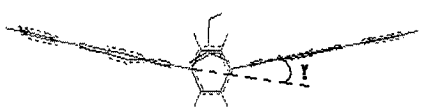
a) Complex with one counterion.

There is a single structure corresponding to the energy minimum (fig.1). In this structure the counterion is coordinated with protons of two successive heterocycles along the chain. The phenyl cycle between them occurs to be rotated on the angle $\Theta \cong 50°$, the chain bends on the angle $Y \cong 25°$ and heterocylces have a mutual CIS orientation.

It should be mentioned that the chain bending can contribute into the flexibility of PBO molecules in solutions [1].



(a)



(b)

Fig1. The structure of the complex with one counterion presented in projections on the plane parallel (a) and ortogonal (b) to planes of the heterocycles.

The position of a counterion is characterized by distances (R1 and R2) between oxygen atoms of the deprotonated acid and protons near the nitrogen atoms.
In the present structure R1=1.53 Å and R2=1.46 Å .

b) Complex with two counterions.

In the structure with the minimal energy (fig.2) one of the counterions (as in the previous case) is coordinated with protons of two successive heterocycles along the chain, i.e. leads as a results to the mutual CIS orientation of heterocycles . The second counterion is localized near the second non-occupied proton of one of the heterocycles. The localization of the first counterion doesn't change practically (R1=1.50 Å , R2=1.47 Å:).

(a) (b)

Fig 2. The structure of the complex with two counterions presented in projections on the plane parallel (a) and ortogonal (b) to planes of the heterocycles.

.

c) Complex with three counterions

. In the most profitable structure (Fig.3) one of the counterions again is coordinated with protons of two successive heterocycles .

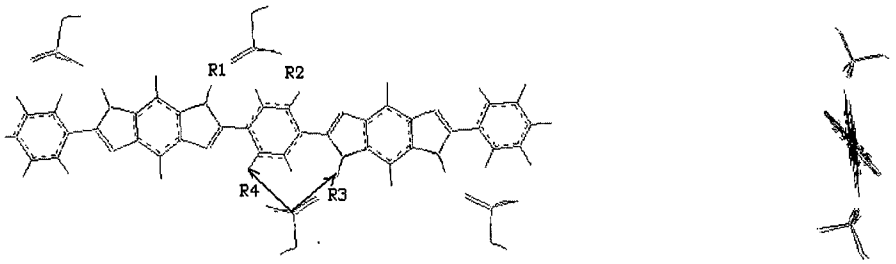
(a) (b)

Fig 3. The structure of the complex with three counterions presented in projections on the plane parallel (a) and ortogonal (b) to planes of the heterocycles.

Therefore the partial condensation of counterions on the protonated molecule leads to the preferable realization of rotational CIS isomers in contrast to the isolated protonated chain where CIS and TRANS have the equal probability.

100% counterion condensation.

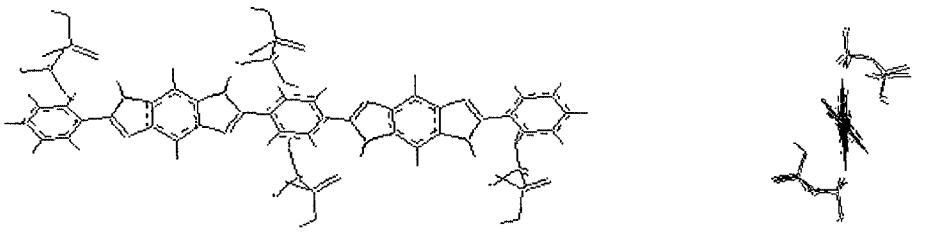
In this case in the most profitable structure (Fig.4) all phenyl cycles are rotated from the molecular plane in one direction (ϕ = 35°). All heterocycles are in the same plane). Counterions are shifted from heterocycles to phenyl rings. Their positions relative to the chain is characterized by the distances between oxygen atoms of the acid and protons near the nitrogen atoms and hydrogen atoms of phenyl cycle (R1,R2 , fig. 4 a), and the distances between thse proon and hydrogen and phosphorous atom of the acid (R3,R4 fig..4 a). In this structure R1=1.47 Å, R2=2.38 Å, R3=3.04 Å, R4= 3.74 Å. The distances between phosphorous atoms of counterions 1 and 2 is equal to 10.4 Å, and between phosphorous atoms of counterions 3 and 4 is equal to 8.6 Å. .



(a) (b)

Fig. .4. The structure of the complex with completely compensated charges of a polyion in projections on the plane parallel to the molecular plane (a) and orthogonal to the molecular axis. (b).

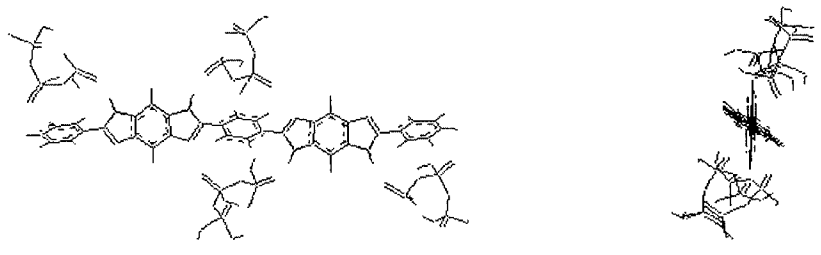
For comparison the structures of complexes for anions of the polyphosphorous acid (n=2 and n=3) are presented in fig.5 and 6.



(a) (b)

(a) (b)

Fig. .5. The structure of the complex with completely compensated charges of a polyion for the case n=2 in projections on the plane parallel to the molecular plane (a) and orthogonal to the molecular axis. (b).



a **b**

Fig. .6. The structure of the complex with completely compensated charges of a polyion for the case n=3 in projections on the plane parallel to the molecular plane (a) and orthogonal to the molecular axis. (b).

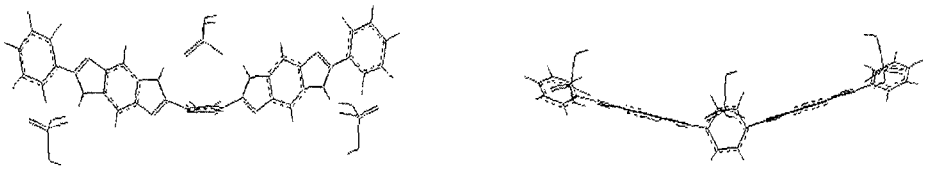
Therefore at partial counterion condensation in the PBO chain containing cis stereo-isomeric heterocycles the CIS rotational isomers are preferable .Chain should bend remarkably. In the same time by the complete counterion condensation the most preferable are TRANS isomers.

2). trans stereoisomers. Complex structure

Partial couterion condensation..

As in the case of molecules containing cis-stereoisomeric heterocycles the most preferable structures for complexes with one, two or three counterions are those where one of the counterions is coordinated with protons of two successive heterocycles along the chain. ,. The phenyl cycle between them occurs to be rotated on the angle $\Theta \cong 50°$, the chain bends on the angle $Y \cong 25°$ and heterocycles have a mutual CIS orientation.

(Fig.7 as an example)



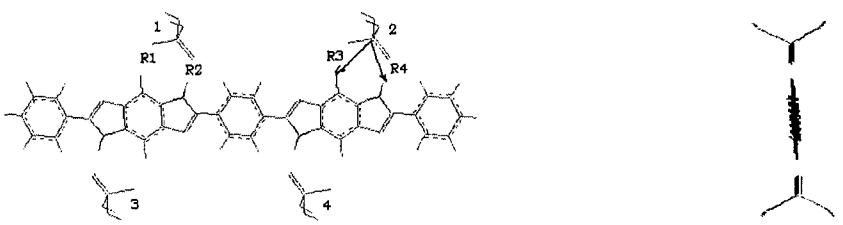
(a) (b)

Fig.7. The structure of the complex with three counterions presented in projections on the plane parallel (a) and ortogonal (b) to planes of the heterocycles.

Therefore as earlier for cis-stereoisomers the partial condensation of counterions on the protonated molecule with trans- stereoisomers leads to the preferable realization of rotational CIS isomers in contrast to the isolated protonated chain where CIS and TRANS have the equal probability.

100% counterion condensation.

The most preferable occurs to be the structure where all cyclic fragments are in the same planer (Fig.8) All counterions are localized near the heterocycles (.R1=1.46Å, R2=2.04Å, R3=2.7Å and R4=3.17Å). Distances between phosphorous atoms of counterions are 12.2 Å between counterions 1 and 2 (3 and 4) 10.4 Å between counterions 1 and 3 and 13.1 Å between counterions 2 and 3



(a) (b)

Fig. 8 The structure of the complex with completely compensated charges of a polyion for the case n=3 in projections on the plane parallel to the molecular plane (a) and orthogonal to the molecular axis. (b).

In this case the most preferable are rotational TRANS isomers of heterocycles.
Details are given in the 9-th quarter report.

2. Effect of the aggregation on the structure of the complex polymer-acid.

We have investigated the effect of the aggregation on the structure of the complex polymer-acid. Aggregates consisting of 2 and 4 complexes were considered. Chains with 100 % charge compensation were considered containing 2,3,4,and 6 monomer units and one additional phenyl cycle (for the symmetry) .Calculations were performed for both cis and trans stereo-isomeric twice protonated heterocycles .The most profitable conformation of a counterion obtained by the AM1 method was fixed and chain parameterswere varied . The structures of aggregates were calculated by the help of MM method by using the same "force-field", as earlier. As a strong acid the polyphosphorous acid was taken (n=1,2,3). Similar calculations were performed for

aggregates of complexes containing not only charged but neutral acid molecules as well (for n=1 and n=2, .

1. Aggregates of two complexes.

Formation of an aggregate doesn't change practically the positions of external counterions. Internal counterions form a common layer and their positions chnge but not enough to disturb Initial ionic pairs . Calculations show that the increase of the acid length and and addition of neutral acid molecules leads to an increase of the distance between complexes in an aggregate.

2. . Aggregates of 4 complexes.

It should be mention that we have failed in some cases to construct the ordered structures for aggregates of 4 complexes , in particular for complexes containing charged and neutral acid molecules and for complexes with twice deprotonated molecules of the polyphosphorous acid (n=3).

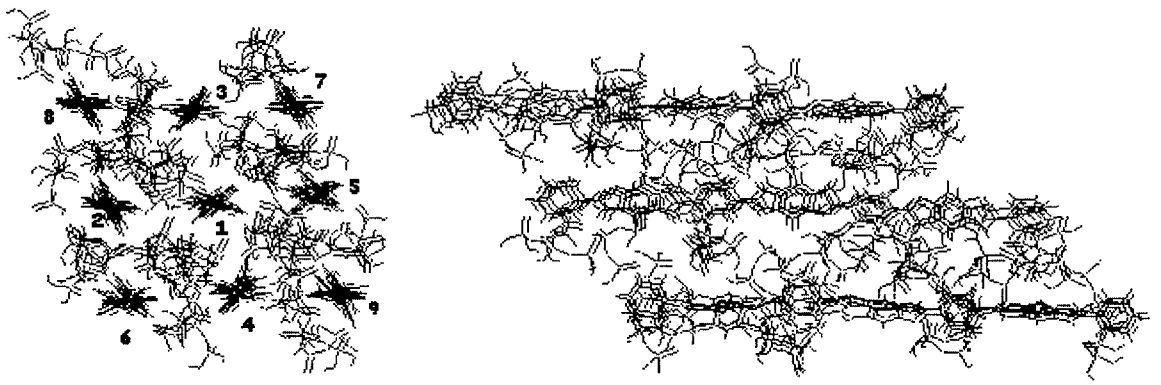
For complexes with charged acid molecules (n=1)the chains in the aggeregate are packed into the rhomb-like cell. The distances between molecular axes occur to be less than those obtained experimentally characteristics of the crystal-solvate of the phase I but larger than those for the phase II [1]).

For the case n=2 these distance are also less than those for the phase I. Only for the case n=3 these distances are close to experimental values..

Detailed information can be found in the 10-th quarter report.

3. The structure of the phase I.

Experimental values of the PBO cell of the crystal-solvate phase I are: a=12.6 Å, b=11.6 Å, c=12.2 Å и γ =98° [10]. The most close to these data characteristics of the packing of the aggregate of 4 complexes were obtained for the complex with anions of the polyphosphorous acid n=3. These results were used for the construction of the model of the packing of 9 complexes: one central molecule and the first coordination sphere (Fig.9). In the process of the minimization in the MM calculations only one restriction was imposed: chain axes should be parallel to each other.



a b.

Fig.9 . The packing of 9 complexes in projections on the planes ortogonal (a) and parallel (b) to the polyions axes..

It was shown that in the phase I the regular mutual orientation of heterocycles characteristic for isolated complexes polymer-acid remains ,i.e. hetercycles have a mutual **TRANS** orientation . The packing of the complexes in an aggregate can be considered as a volume-centred packing of polycations in the relatively isotropic matrix of counterions Cell parameters : **a**=12.4 Å and

b = 11.2 Å .
We can conclude that the degree of the polymerization of the polyphosphorous acid which anions participate in the formation of the phase I is not less than 3.
These calculations were performed in the 12-th quarter

4. Mechanism of the transition from the phase I to the phase II.

By the 100% counterion condensation the part of the space near the polyion remains to be free and therefore additional charges could join to a chain

a) *Joining of additional (relative to the 100% condensation) counterions to the polyion.*

At first the possibility of the joining of the additional charge was studied for the chain consisting of 2 monomer units. It occurred that additional counterions are attracted to the neutral complex and coordinate with hydrogen atoms of the heterocycle and phenyl cycle where the part of the positive charge received my the molecule by the protonation is localized
The energy gain by the joining of one additional counterion is equal to 40.2 kcal/mole, and by the joining of the second additional counterion the additional gain is equal to 21.9 kcal/mole . Therefore the total energy gain by the addition of two counterions is 62.1 kcal/mole . The structure of such a complex is shown in the fig.10..

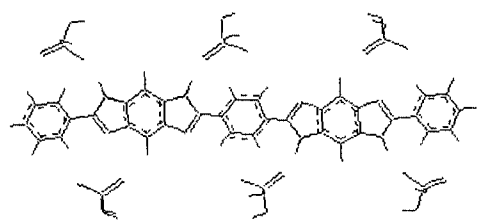


Fig.10 The structure of the complex with two excess counterions.

Similar calculations were performed for protonated chains consisting of 3,4 and 6 monomers.
It was shown that the most profitable situation is realized when additional counterions join to the chain over the monomer , i.e, one additional charge per two monomers.

b) *Interaction of two complexes with an excess charge*

The calculations were performed for two complexes .Each complex contained a chain (two twice protonated heterocycles and three phenyl cycles) and 6 anions of the ortophosphorous acid. Two complexes were placed at some distance R between chain axes . The energy minimization was perormed at fixed R by the variation of all other parameters.

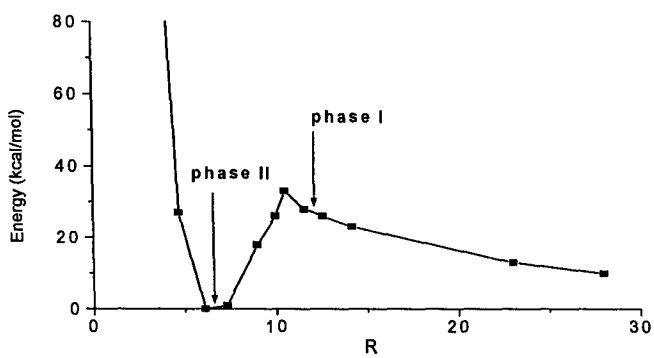


Fig.11. Potential curve for two complexes with an excess charge located at different distances

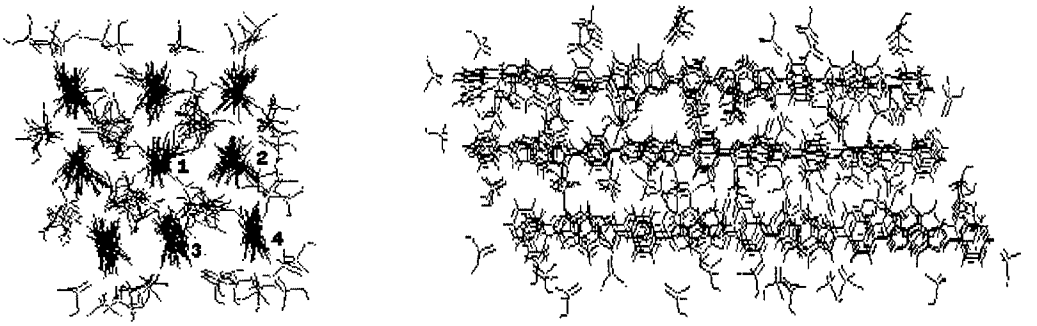
It was shown (Fig.11) that there is a potential well at short distances corresponding to the attraction. At distances exceeding 10.5 Å the complexes repel each other. It occurs that the distances corresponding to the repulsion region are characteristic for the phase I. The distances characteristic for the phase II are in the attraction region. We believe that namely the overcharging mechanism is responsible for the formation of the crystal-solvate phase II and its microfibrillar structure.

Detailed information is presented in 10-th and 11-th quarter reports.

5. The structure of the phase II.

It was assumed that the phase II is formed by complexes with an excess charge because an addition of the large amount of water leads to the formation of many co-ions due to the dissociation of the acid in the water. The calculations of the packing of two complexes with an excess charge due to the additional condensation of anions of orto-phosphorous acid have given the distances between chain axes close to experimental parameters for the phase II (a= 7.0 Å, b= 5.8 Å, γ =99° [10])

.These results were used for the calculation of the packing in the aggregate of 9 molecules similar to the previous one (see part 3 of this chapter) but with an excess charge. (Fig.12)..



a) b)

Fig.12 . The packing of 9 complexes with an excess charge in projections on the planes ortogonal (a) and parallel (b) to the polyions axes.

The regular mutual orientation of the heterocycles along the chain characteristic for an isolated complex and for the phase I is disturbed for this aggregate. That agrees with experimental data [8] which indicate that the structure of the phase II is less ordered than the phase I. Character of the packing is determined by the acid anions.They are localized in the central part of the cell. The averaged over 4 cells values of parameters a= 6.85 Å, b= 6.0 Å and γ =105° are close to the experimental ones :.a= 7.0 Å, b= 5.8 Å, c=12.0 Å и γ =99° [8]

These calculations were performed in the the12-th quarter t.

Chapter Y. Crystalline structure of neutral polymer PBO .

We have performed the calculations of the packing of PBO molecules untreated by the acid in the crystalline cell by the MM method. The force-field was used with potential parameters giving the best agreement between results of AM1 and MM calculations (see chapter I) .

Chains with 3 and 6 monomeric units were considered. Every domain consisted of one central molecule and three coordination spheres.

16 different variants of structures were calculated :

1. Two types of mutual placement of heteroatoms in one cyclic fragment-**cis** and **trans** stereoisomers.
2. Two types of mutual orientations of heterocycles along the chain (rotational isomers **CIS** and **TRANS**).
3. Four variant of the relative shift of chains in the layers along the long molecular axis:
Either all chains are shifted in one direction (+Δ or -Δ), or shifts alternate –in one direction (+Δ), than in another direction (-Δ).
4. Chains can be oriented parallel or antiparallel to each other.

For all variants calculations were performed for 2, 4, 9, 25 и 49 chains.

Main results are presented in the Table 1.

Structures where all chains are shifted in one direction are marked by the number 1. The structures with the alternating shift are marked by the number 2.

Parameters of the packing:

1. Parameters of the elementary cell **a** and **b** corresponding to the distances between long axes of molecules in the plane normal to these axes.
2. Shifts along the plane c in planes ac Δac and bc Δbc
3. Angle between the axesof the primitive cell γ ,
4. Angle of the rotation of the molecular plane from the **ac** plane Θ
5. Energy of the packing(per one monomer unit) in the elementary cell –**E**

All linear sizes are given in nanometers, angles in grades and the energy –in kcal/mole

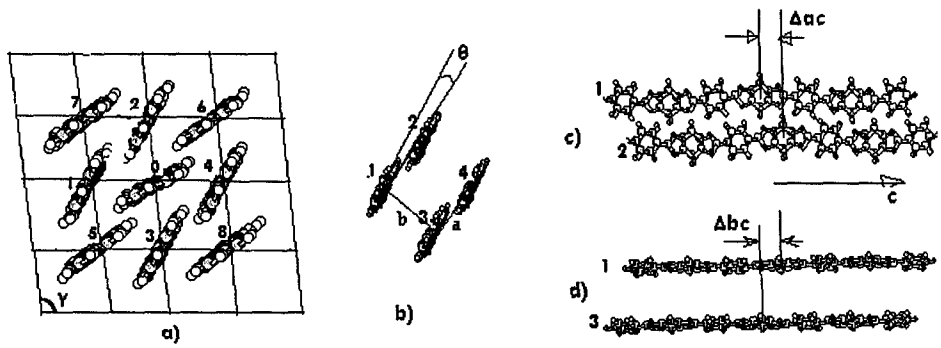


Fig.12. Domain containing 9 molecules (a) and its fragments (b), (c) and (d).

Table 1.

	a	b	c	Δac	Δbc	γ	Θ	E
Trans-TRANS I Parallel								
1.a	0.643	0.619	1.216	0.21	0.6.02	92.3	0	-18.64
1.b	0.571	0.694	1.216	0.319	0.004	101.6	20.5	-18.31
2	0.599	0.670	1.216	0.213	0.595	97.4	21.3	-18.34

Trans-TRANS II Antiparallel								
1	0.568	0.697	1.216	0.322	0.006	101.9	20.5	-18.2
2	0.566	0.691	1.216	0.332	0.487	100.7	20.7	-18.94
Trans-CIS III Parallel								
1	0.568	0.703	1.215	0.312	0.006	102.6	22.5	-17.53
2	0.599	0.674	1.215	0.305	0.500	98.6	19.5	-18.28
Trans-CIS IV Antiparallel								
1	0.563	0.706	1.215	0.319	0.015	102.3	22.4	-18.02
2	0.593	0.682	1.215	0.31	0.505	98.4	20.3	-18.4
Cis-TRANS V Parallel								
1	0.584	0.679	1.215	0.296	0.03	98.5	19.5	-17.69
2	0.589	0.678	1.215	0.285	0.112	100.8	17.5	-18.92
Cis-TRANS VI Antiparallel								
1	0.578	0.684	1.215	0.316	0.022	101.2	19.2	-17.53
2	0.583	0.683	1.215	0.279	0.119	100.9	17.0	-18.68
Cis-CIS VII Parallel								
1	0.569	0.707	1.213	0.292	0.03	106.8	22.3	-17.4
2	0.543	0.690	1.213	0.29	0.025	106.9	15.5	-15.97

Chain conformations in all structures remain flat , i.e. all cyclic fragments are in the same plane. One could expect that for structures where all molecules are shifted equally both directions of the shift should be equivalent. It occurred to be correct for all structures except one of them for parallel trans-TRANS chains. In this case by the shift in one direction oxygen atoms occur to be close to each other. By the shift in another direction nitrogen atoms are in the close contact. Due to this non-equvalence of shifts $+\Delta$ and $-\Delta$, two different types of packing are formed. If oxygen atoms are close to each other the molecular planes are oriented parallel to each other (fig .13)

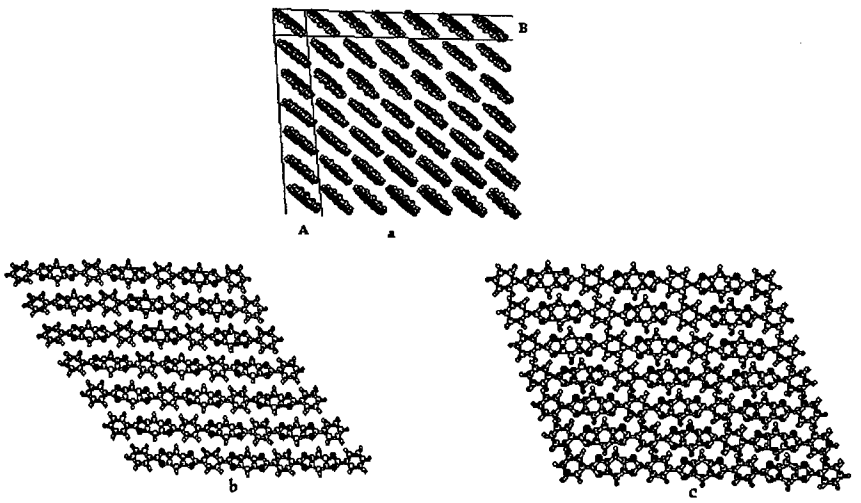


Fig13. Domain containing 49 molecules (one central molecule and 3 coordination spheres Projection on the plane normal to the long axes of molecules (a), Packing in layers A (b) and B(c).

In the case when nitrogen atoms are close to each other the parquet-like packing is formed where molecular planes are rotated relative to each other in different directions (Fig.14)

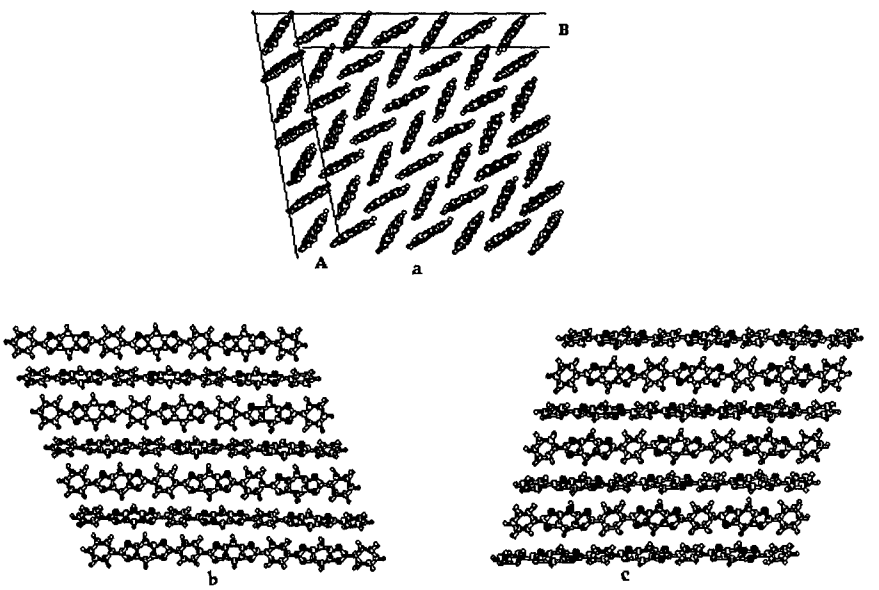


Fig.14. Domain containing 49 molecules

In both cases the volume-centered packing of molecules was formed. In this type of packing every elementary cell contains two molecules. The energy per one unit occurred to be 0.33 кcal/mole lower for the packing with parallel molecular planes
In all other structures the volume centered type of the packing with the parquet –like mutual orientation of molecular planes is obtained.
As an example see the fig.15.

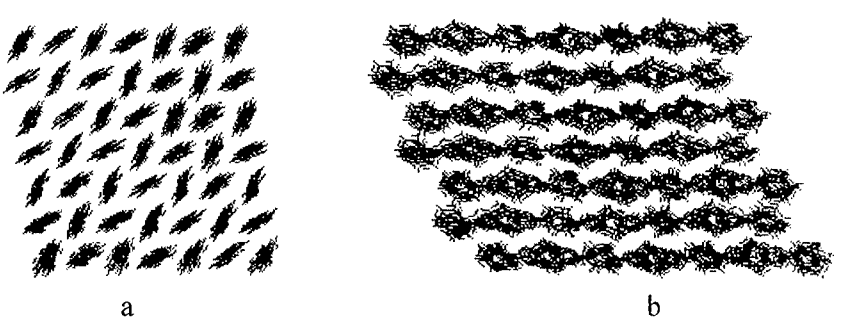


Fig.15. Domain of 49 cis-TRANS molecules with the alternating shift..

The important difference of **cis-CIS** molecules from other types of molecules is their curvilinear geometry. The energy minimum obtained by the AM1 method corresponds to . a bow-shaped chain with cyclic fragments in the same plane. In [28], for the determination of the packing of PBO molecules (cis stereoisomers) corresponding to experimental X-ray data the

parallel orientation of flat linear molecules was chosen. As our calculations show such a packing is possible only for **trans-TRANS** molecules and not in all cases.
As a whole we can conclude that calculated cell parameters given in the Table I are close to experimental data **a**=0.56 **b**=0.708 **c**=1.205 γ= 101,2 [28.29].

In fact it is not correct to believe that in the real PBO molecule (it concerns both **cis** and **trans** stereoisomers) only one type of rotational isomers is realized. The calculations by the AM1 method show that intramolecular energies of molecules consisting only either of **TRANS** rotational isomers or only of **CIS** rotational isomers are the same practically. Therefore the real molecule can be considered as a statistical "copolymer " of different rotational isomers. It is necessary to consider mixed or defected situations.

Preliminary calculations for defected packings of **cis** stereoisomers gave interesting results. Two cases were considered.

1. We have substituted the central molecule in the domain formed by 9 parallel **cis-TRANS** molecules by the **cis-CIS** chain and performed the minimization of the total energy by variation of all parameters. It turned out that the surrounding deforms the **cis-CIS** chain and it takes a rectilinear shape instead of the bow-shaped one. At the same time the cell parameters change (a=0.582, b=0.647). Due to the softness of the deformation potentials for a PBO molecules the loss of the packing energy per one monomer occurs to be not large and is equal to $\approx$ 0.33 κcal/mole.

2. Similar calculations were performed for a domain consisting of 9 **cis-CIS** molecules.. In this case the central chain was substituted by a **cis-TRANS** molecule. It turned out that the surrounding deforms the central chain and but it takes a bow-shaped shape instead of the rectilinear one. The cell parameters also change slightly (a=0.58, b=0.665). The energy loss is also small ($\approx$ 0.5 κcal/mole)

We see however that cell parameters for defected structures occur to be in the same range as for ideal structures.

Details are given in the 7-th and 8-th quarter reports

• Conclusions

1. Effect of the protonation on the conformation and structure of PBO molecules in the solution

It was shown that results obtained for one monomer unit [1] can not be approximated on the long PBO chain . In the chain every phenyl cycle is surrounded by protonated heterocycles . It effects not only the equilibrium conformation (for four times protonated heterocycles) but also the height of the barrier of the internal rotation. The protonation leads to the decrease of this barrier in contrast to the prediction of 1]. In the same time for the partially protonated molecules the protonation leads to a strong increase of the barrier relative to neutral molecules..

Another factor which effects the chain conformation of PBO in strong acids are counterions. They can form ionic pairs with charges on the protonated PBO molecule. In the case of the partial condensation of counterions the most favorable one occurs to be a bended conformation of the chain with preferable rotational CIS isomers.

The calculated phase diagram of the PBO solution in strong acids predicts the transition into aggregated state by the concentration increase at concentration values close to the experimental ones. The calculations were performed for the model assuming the formation of ionic pairs and tetramers with the growth of the concentration. At the water addition the aggregation occurs at lower polymer concentration in agreement with experiment.

The formation of the LC phase in PBO solutions was considered as a result of the concurrence between electrostatic repulsion of charged polyions and attraction due to the ionic pairs formation. Two ordered phases were predicted . The concentration interval of their coexistence was determined. Its lower boundary corresponds to experimental value of the concentration of the LC ttansition and the upper one –to the aggregated state of the PBO .

2. The influence of strong acids on the conformation of PBO chains in a crystalline state.

There are two crystal-solvate phases including acid molecules: phase I and phase II. Phase I is formed from the solution either at some concentration or by the addition of a small amount of water.[10]. Transition into the phase II occurs by the addition of a large amount of water (>7%) [10]. The first phase is a macrophase one and the second phase appears by the microphase separation of the system.
In both phases the PBO molecules are protonated .Therefore they consist of the complexes containing the PBO polycations and acid anions.

1) The phase I was assumed to be formed by the complexes with completely compensated charge. It was shown that TRANS isomers are the most profitable ones for successive heterocycles along the chain .

The mutual orientation of heterocycles in the phase I is the same as in the isolated complexes polymer+acid. The phase structure is a volume-centered packing of polycations in the isotropic matrix of acid anions. Calculated cell parameters are close to experimental values.

2.) The joining of additional counterions to the complex with 100% counterion condensation occurs to be energetically favorable. Excess counterions are coordinated with hydrogen atoms of the cyclic units. Such conditions arise for PBO molecules by the water addition to the solution in the strong acid.

Distance dependence of the energy of the interaction of two complexes with an excess charge shows the minimum at short distances and repulsion at large distances. It was shown that characteristic distances for the phase I correspond to the repulsion region and those for the phase II to the attraction region. It was concluded that namely the overcharging mechanism is responsible for the formation of the crystal-solvate phase II and its microfibrillar structure.

The phase II occurred to be less ordered than the phase I in agreement with experimental data. In particular the regular mutual orientation of heterocycles along the chain characteristic for the phase I is absent in the phase II. Only the order in the positions of molecular axes remains. The calculated cell parameters are close to experimental values. Acid anions are localized in the central part of the cell.

3. Packing of neutral PBO molecules in the crystal.

Independent on the stereoisomeric composition the volume-centered packing of molecules is formed. Every elementary cell contains two molecules. Chain conformations are flat. For all types of molecules (except one) the parquet-like type of the mutual orientation of molecular planes is realized. Only for trans-stereoisomeric molecules the parallel type of the mutual orientation is also possible. Cell parameters are not far from experimental data.

- **References :**

[1] *Farmer, B.L.; Dudis, D.S.; Adams, W.W.* // Polymer. 1994. V. 35. N. 17. p. 3745.
[2] *Farmer, B.L.; Chapman, B.R.; Dudis, D.S.; Adams, W.W. Polymer 1993, V.34, N. 8, p. 1588*

[3] *Lee, C.C.; Chu, S.G.; berry, G.C.* // J. Polym. Sci., Polym. Phys. Edn. 1983. V.21. N. 6. p.1573.
[4] *Chu, S.G.; Venkataraman, S.; Berry, G.C.; Einaga, Y.* // Macromolecules. 1981. V.14. N.4. p. 939.
[5] *Cohen, Y.; Cohen, E.* // Macromolecules. 1995. V.28. N. 10. p. 3631.
[6] *Adams, W.W.; Eby, R.K.; McLemore D.E. (Eds)*// The Material Science and Engineering of Rigid-rod Polymers, Materials Research Simposium proceedings. 1989. V.134. Chapters 5 and 6.
[7] *Won Choe, E.; Sang Nim Kim* // Macromolecules. 1981.V.14. N.4. p. 920.
[8] *Wolf, J.F.; Loo, B.H.; Arnold, F.E.* // Macromolecules. 1981. V.14. N.4. p. 909.
[9] *Tsabba, I.; Rein, D. M.; Cohen, Y.* // Journal of Polymer Science: Part B: Polymer Physics. 2002. V. 40. p.1087.
[10] *Cohen, Y.; Adams, W.W.* // Polymer. 1996. V.37. N. 13. p. 2767
[11] Y. Cohen, E.Cohen Macromolecules,1995, 28,3631-3636.
[12] B.-Y. Ha, Andrea J.Liu Physical Rev. Letters 1997,v.79, N7, 1289; 1998, v.81, N5, 1011.
[13] B.-Y. Ha, Andrea J.Liu Physical Rev. E. 1999, v.90, N1, 803
[14] J. Ray, G.S.Manning Langmuir 1994, 10,2450.
[15] J. Ray, G.S.Manning Macromolecules 2000, 33,2901..
[16] J.-F. Joanny Polymer 1980,21,71.
[17] E.Yu. Kramarenko, I.Ya. Erukhimovich, A.R.Khokhlov Macromol. Theory and Simul. 2002, 11, 462.
[18] Onsager, Ann. N.Y. Acad. Sci. 51,627, 1949.
[19} I.A.Nyrkova, N.P.Shusharina, A.R.Khokhlov Macromol Theory and Simul. 1997, 6, 965.
[20] I.I.Potemkin, R.E.Limberger, A.N.Kudlay, A.R.Khokhlov Physical Review 2002, 66, 11802.
[21] E.Won Choe, Sang Nim Kim Macromolecules, 1981, 14, 920.
[22] Khokhlov A.R. The Doctor thesis (Moscow, 1985)
[23] V.Yu.Borue and I.Ya. Erukhimovich 1988, Macromolecules, v.21, N 11, 3240-3248.
[24] R.M.Nyquist, Bae-Youn Ha, A.J.Liu 1999, Macromolecules, v.32, N10, 3481-3487.
[25] F.Oosawa, Polyelectrolytes, Marsel Dekker, Inc., New York, 1970.
[26] Cohen Y., Saruyama Y. and Thomas E.L. Macromolecules 1991, v. 24, 1161.
[27] Ha B.-Y. And Liu A.J. Physical Review Letters 1998, v.81, N 5,1011.
[28] Kohji Tashiro, Junichi Yoshino, Tooru Kitagawa, Hiroki Murase, Kazuyuki Yabuki, Macromolucules,1998,31,5430.
[29] Fratini A.V. in "The Material Science and Engineering of Rigid-Rod Polymers (Eds.W.W.Adams, R.K. EbyD.E. McLemore) Materials Research Society Symposium Proceedings, 1989, v. 134, p.43.

- **List of published papers and reports with abstracts**

N.Lukasheva,A.Darinskii , Effect of the protonation on the conformations of rigid-rod polymers . 2005, submitted to .Polymer Science

Abstract:

It is well known that by the dissolution of rigid polymers in strong acids leads to their protonation. The effect of the protonation on the chain conformation is studied for one of the typical representative of these polymers the poly(para-phenylene-benzobioxazol)(PBO). In contrast to [7} where the model of the monomer unit of PBO consisting of the heterocycle and the phenyl cycle was considered , we have considered model molecules exceeding the monomer unit and containing three and more cyclic fragments. The calculations of the barriers

of the internal rotation for twice and four times protonated molecules where the heterocycles are protonated on two sides of the phenyl cycle give a result opposite to that obtained in [7]. The protonation leads not to an increase but to a decrease of the barrier for such molecules. In the same time in molecules where only the heterocycle on one side from the phenyl cycle is protonated the protonation leads to strong increase of the barrier height . For the estimation of the effect of the protonation on the bending flexibility of macromolecules it is enough to consider the monomer unit only.

- **List of presentations at conferences and meetings with abstracts**

1. **N.Lukasheva**,A.Darinskii, Mechanisms of Aggregation and Nanostructure Formation in Solutions of Rigid-Rod Polymers in Strong Acids,
Proc. 12 International Conference on Composites/Nanoengeneering, 1-6 August 2005, Tenerife, Spain

Abstract:

MECHANISMS OF AGGREGATION AND NANOSTRUCTURE FORMATION IN SOLUTIONS OF RIGID-ROD POLYMERS IN STRONG ACIDS.

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St.Petersburg, Russia

Rigid –rod polymers received much attention because of their thermal/oxidative stability, environmental resistance and of their high mechanical properties resulting from their inherent molecular modulus and from their degree of molecular orientation achieved by fibre spinning from liotropic liquid crystalline solutions. However many rigid-rod polymers such as PBO are soluble only in very strong (Lewis) acids from which they could be processed into final product.
The dissolution is accompanied by the protonation of macromolecules. It is well known [1] that such polymers transform into a condensed state either at the definite polymer concentration (~ 20%) or at the addition of water that shifts the transition into the aggregate state to lower polymer concentrations. It was found [2] that the addition of a very small amount of water (about 1%) results in the formation of the crystal-solvate phase (Phase I). Moreover at an addition of the sufficient amount of water the formation of nanoscale fibrils with a diameter about 10 nm (Phase II) was observed [2]. Similar microfibrillar morphology is observed in the oriented PBO fibre coagulated by immersion in water. In spite of wide applications the physical origin of these processes isn't well understood till now.
In the present study the mechanisms of the aggregation (**I**) and fibrils formation (**II**) are suggested.

I. It was supposed that the aggregation is caused by the decrease of the dielectric constant in the solution by the increase of the concentration and as a result the formation of ionic pairs between protons and counterions. Authors have used the theory developed by Kramarenko et al. [3]
Formation of ion pairs and multiplets (quadrupoles) was described as reversible reactions with the corresponding association constants depending on the energy of interactions between charges that in turn depends on the dielectric properties of the medium.
The calculations of the phase diagram of the polyelectrolyte solution with parameters corresponding to the di-protonated PBO solution in strong acids were performed. The cases of equal association constants for ion pair and tetramer formation as well as different values of these constants were analyzed. Calculations have shown that the characteristic polymer concentrations corresponding to the beginning of the aggregation are in the experimental region of the concentrations for PBO solutions.

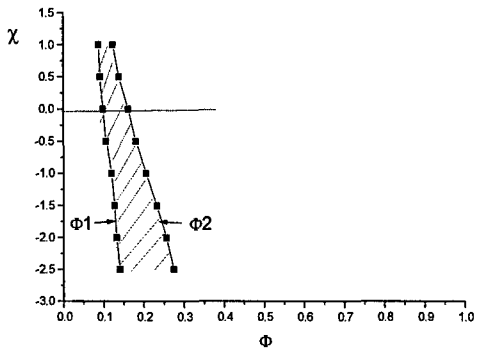


Fig.1. Phase diagram of PBO solution in a strong acid. χ- Flory-Huggins interaction parameter and Φ-polymer concentration.The phase coexistence region is shown as a hatched region.

The calculations of the fraction of free ion pairs (p) and the fraction of ion pairs in multiplets (q) as the functions of polymer concentration have shown (Fig.2) that the aggregation takes place at $q<1/3$.

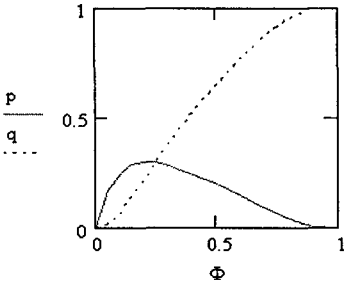


Fig.2. The fractions of free ion pairs (p) and the ion pairs in multiplets (q)

Polymer molecules precipitate in the form of the complexes between the protonated PBO polycations and acid anions. For the same model the effect of the addition of small amount of water to the PBO solutions in strong acids on the aggregation process was analyzed. It was shown that this addition leads to the shift of the aggregation region to smaller concentrations. This result is also in agreement with experimental data for the system considered

II. The presence of water leads to an additional dissociation of acid molecules and appearance of large amount of co-ions [1]. Our calculations of the structure of the complexes between di-protonated PBO polycation (Fig.3) and phosphoric acid anions (Fig.4)

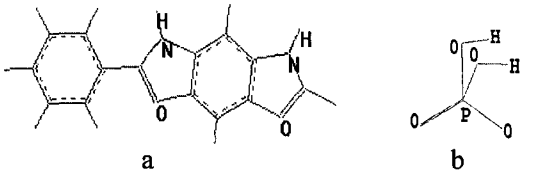


Fig.4. Chemical structures of the di-protonated PBO monomer (a) and of the phosphoric acid anion.

and the structure of aggregates of two such complexes performed on the base of quantum chemistry (AM1) and molecular mechanics methods have shown that the addition of co-ions to the complex with 100 % compensation of the charge is energetically favorable Therefore under the conditions of the excess amount of counterions the complex can be formed which contains polyion and counterions with an overall charge exceeding the charge necessary for the neutralization of the polyion charge (overcharging effect). Example of the minimum energy structure of such a complex with the total charge –1 per monomer is shown in Fig.5.

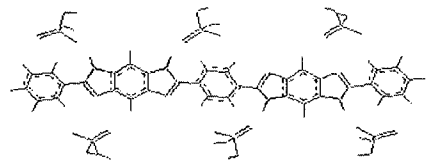
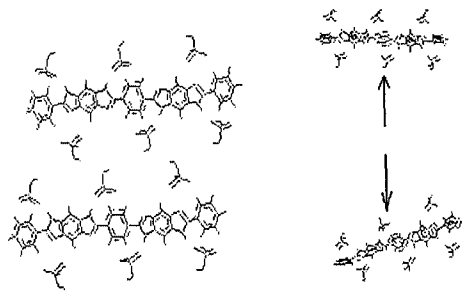


Fig.5. Minimum energy structure of the overcharged complex.

It was shown that the complexes with an excess charge interact as a whole and repel each other if they are situated at distances corresponding to the phase I where the counterion shells don't overlap. Fig.6 illustrates this case.



a b

Fig.6. Two complexes situated at a distance 11.6 Å(a) and the resulting structure (b).

However complexes attract each other if they are located at distances corresponding to the overlapping of their counterion shells (Fig.7). These distances occurred to be close to experimentally observed for the microfibrillar structures in PBO.

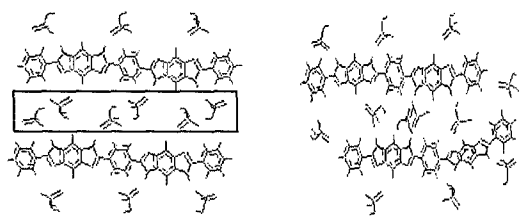


Fig.7. Two complexes situated at the distance 6.5 Å (a) and the resulting structure (b).

Therefore the potential surface has two minima. One of them corresponds to the case when complexes are distanced. And the other minimum is at the intermolecular distance of the crystal-solvate phase II. Potential curve obtained from the minimization of the interaction energy of two overcharged complexes placed at a number of fixed distances is presented in Fig.8.

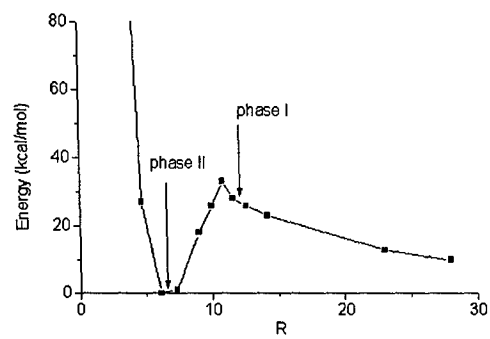


Fig.8. Potential curve for two complexes located at different distances

We believe that namely the overcharging mechanism is responsible for the formation of the crystal-solvate phase II and its microfibrillar structure..

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References :

1.Y. Cohen, E.Cohen Macromolecules, 28,(1995) ,3631-3636.
2. Y. Cohen, W.Adams, Polymer, 37 (1996), 1886.
3. E.Yu. Kramarenko, I.Ya. Erukhimovich, A.R.Khokhlov ,Macromol. Theory and Simul. 11 (2002), , 462.

2. **N.Lukasheva**,A.Darinskii, Effect of Protonation on Rigid Polymers in Solutions of Strong Acids, 5-th International Conference "Molecular Order and Mobility in Polymer Systems", 20-24.6.2005, St.Petersburg. P-051

Abstract:

Effect of protonation on rigid polymers in solution of strong acid

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Many rigid-rod polymers(such as poly(*p*-phenylene benzobisoxazole), PBO) can be dissolved only in strong protonating acids, i.e. the protonation is a precondition to dissolution. The protonation can change the chain conformation in comparison to the neutral chain. In [1] the calculations on the base of semi-empirical AM1 calculations have shown that the protonation of a PBO molecule leads to the strong (about 3 times) increase of the barrier of the internal rotation around the bond connecting neighboring cycles. These calculations were performed for the fragment of the PBO chain consisting of one diprotonated heterocycle (He) and one phenyl (Phe) cycle. However in the PBO chain charged heterocycles are situated on each side of the phehyl ring. That is why we have performed AM1 calculations for a fragment (He-Phe-He) with diprotonated heterocycles . It occurred that in this case the barrier doesn't increase but even slightly decreases in comparison to the neutral fragment. The increase of the length of the fragment (He-Phe-He-Phe-He) doesn't change this conclusion.
The analysis shows that the main reason of such a behavior is a redistribution of charges on the atoms by the internal rotation and as a results the change the energy of Coulomb interactions . It is interesting that the protonation of only one heterocyclic neighbour of a phenyl ring in the fragment (He-Phe-He) leads to even larger increase of the barrier than in the protonated fragment (He-Phe).

1. B.L.Farmer,D.S.Dudis and W.W.Adams,Polymer,1994,35,17,3745

- **Information on patents and copy rights**

No patents were submitted in frame of this project.

Signatures:

Project manager: N.V.Lukasheva

Signatory of the Project Agreement:

Director of IMC RAS **member -correspondent of RAS**
Prof.E.F.Panarin